

# PATENT SPECIFICATION

1,102,903



NO DRAWINGS

1,102,903

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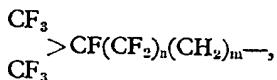
**Int. Cl.:**—C 07 c 53/32, C 07 c 69/62, C 07 c 103/72, C 07 c 119/04, C 07 d 23/06,  
C 07 d 55/12

## COMPLETE SPECIFICATION

### Fluoro Alkyl-Containing Compounds and Water- and Oil-Repellent Compositions containing them

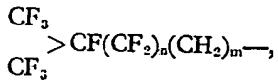
We, DAIKIN KOGYO KABUSHIKI KAISHA, a Japanese Body Corporate, of Shin-hankyu Building, 8 Umeda, Kita-ku, Osaki-shi, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

5 This invention relates to a series of fluorine-containing compounds having a group of the formula



10 n being an integer from 2 to 20 inclusive and m being 0 or an integer from 1 to 20 inclusive, bonded to one end position. The invention further pertains to the water-repellent and oil-repellent compositions containing any of said compounds as a main effective ingredient.

15 The present inventors have found that a series of compounds having a branched-chain fluoroalkyl group of the formula



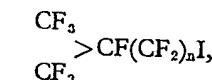
20 n and m being as defined above, is exceedingly useful as a water-repellent and oil-repellent agent. Namely, the compositions comprising any of said compounds as a main effective ingredient impart to the articles treated therewith a markedly high order of water-repellency

and oil-repellency. Said branched-chain fluoroalkyl-containing compounds further are soluble not only in a fluorine-containing organic solvent, such as trichlorotrifluoroethane, but in conventional solvents, such as ethers or ketones, so that the resultant compositions can be easily prepared into the form of a solution, having a wide range of application. Said branched-chain fluoroalkyl-containing compounds, furthermore, can be synthesized in a simple manner and in a high yield, because the starting materials of the formula

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35

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45 n being as defined above, which starting materials when n is an even integer may be



prepared by telomerizing



50  $\text{CF}_2 = \text{CF}_2$  are low in melting point and the distribution of the molecular weight thereof can be easily controlled. Such specific features of the branched-chain fluoroalkyl-containing compounds of this invention becomes more apparent when compared with the corresponding compounds having a straight-chain fluoroalkyl group of the formula  $\text{CF}_3(\text{CF}_2)_c(\text{CH}_2)_d—$ , c being in integer from 14 to 22 inclusive and d being 0 or an integer from 1 to 20 inclusive.

55 It is accordingly one object of this invention to provide a new series of fluorine-containing compounds having bonded to one end

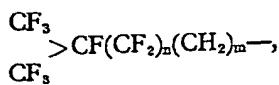
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position a branched-chain fluoroalkyl group of the formula



n and m being as defined before.

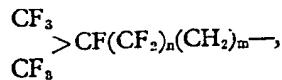
5 Another object of the invention is the provision of a new series of water-repellent and oil-repellent compositions containing any of the aforesaid compounds as a main effective ingredient.

10 A further object of the invention is the provision of the aforesaid water-repellent and oil-repellent compositions having an ability to impart to the articles treated therewith a markedly high order of water-repellency and oil-repellency.

15 A still further object of the invention is the provision of profitable processes for imparting to the articles to be treated an improved order of water-repellency and oil-repellency with said compositions.

20 A still further object of the invention is the provision of profitable processes for the production of the aforesaid branched-chain fluoroalkyl-containing compounds.

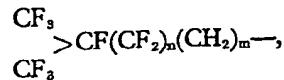
25 All of the fluorine-containing compounds of this invention have bonded to one end position a branched-chain fluoroalkyl group of the formula



n being an integer from 2 to 20 inclusive and m being 0 or an integer from 1 to 20 inclusive.

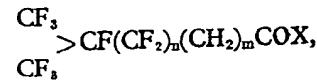
The representative instances of the fluorine-containing compounds having a branched-chain fluoroalkyl group of this invention can be classified as follows:

Group A: In this group are included the fluorine-containing compounds having bonded to one end position a branched-chain fluoroalkyl of the formula

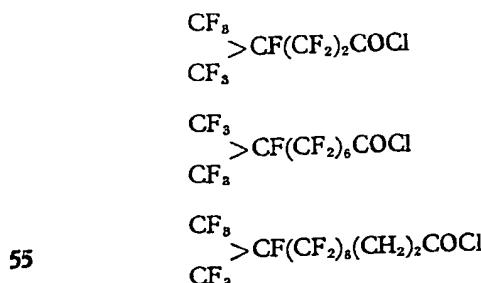


n and m being as defined before, and having attached to another end position a group which is capable of forming a chemical bond with a hydroxy, carboxyl or an amino group. The compounds of this group are accordingly subdivided into the following groups:

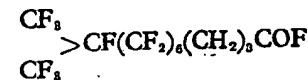
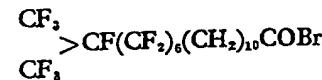
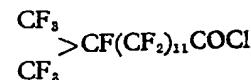
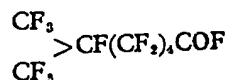
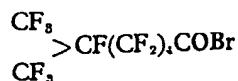
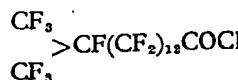
Group A-1: This group consists of the compounds of the formula

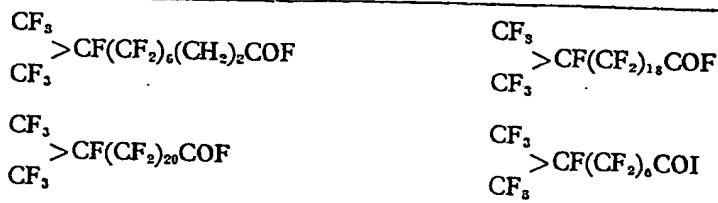


n and m being as defined before and X a halogen atom:

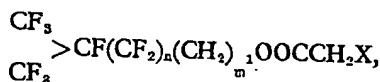


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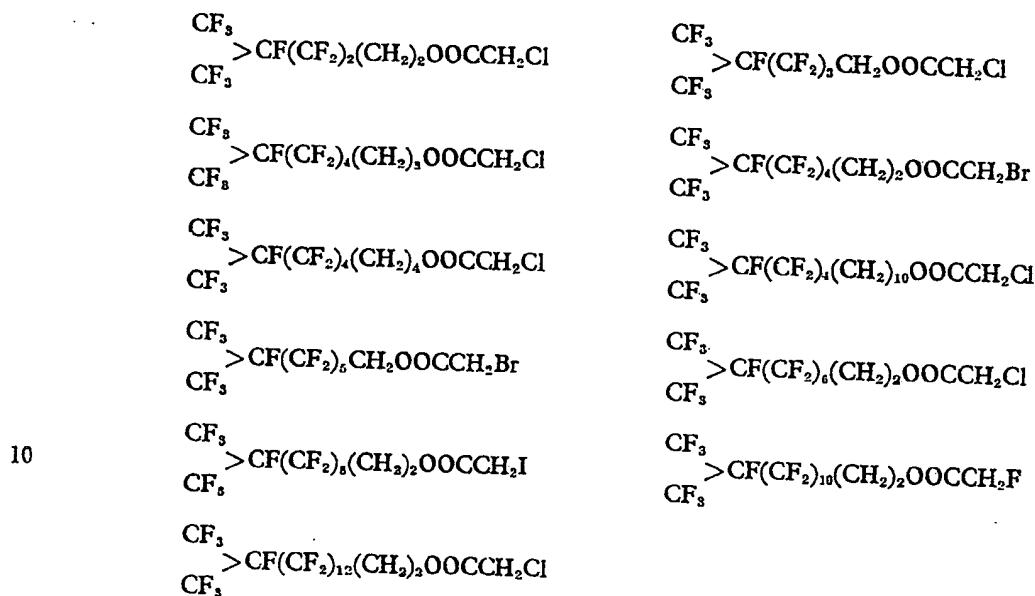




*Group A—2:* The compounds belonging to this group are of the formula:



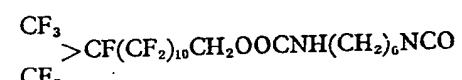
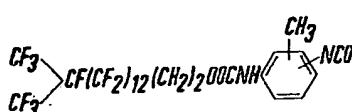
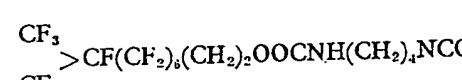
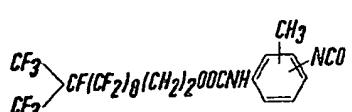
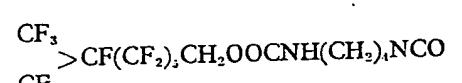
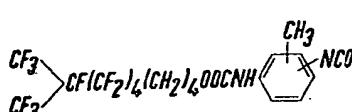
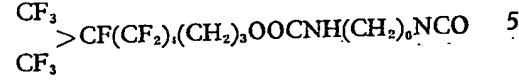
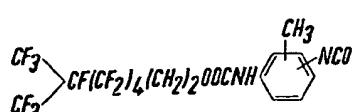
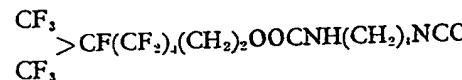
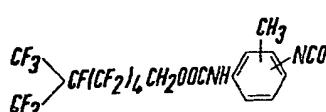
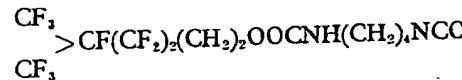
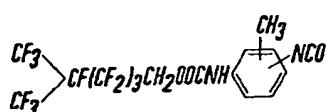
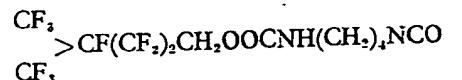
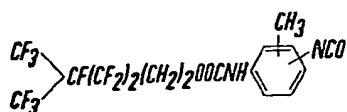
5 wherein  $m^1$  is an integer from 1 to 20, and  $n$  and  $X$  are as defined before:



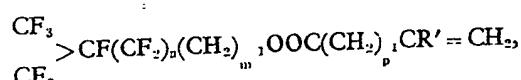
*Group A—3:* The compounds belonging to this group are of the formula



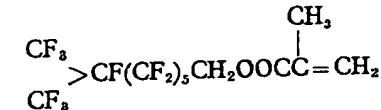
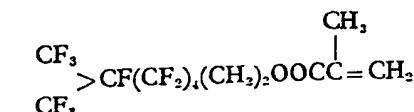
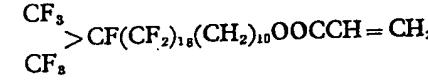
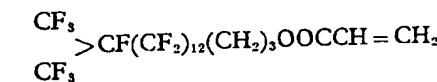
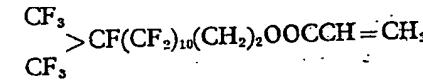
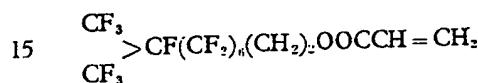
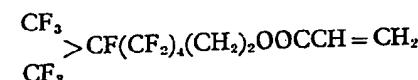
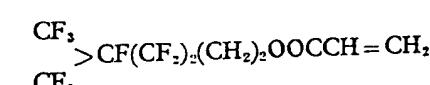
15  $Y$  being an alkyl group having from 1 to 3 carbon atoms, and  $k$  being an integer from 2 to 10; and  $n$  and  $m^1$  are as defined before:



10 *Group A-4*: The compounds belonging to this group are of the formula

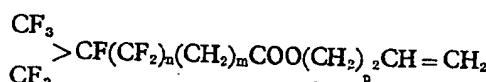


wherein  $\text{R}'$  is  $-\text{H}$  or  $-\text{CH}_3$ ,  $p^1$  is an integer from 0 to 20, and  $n$  and  $m^1$  are as defined before:



	$\text{CF}_3 > \text{CF}(\text{CF}_2)_8(\text{CH}_2)_2\text{OOCC}=\text{CH}_2$	$\text{CF}_3 > \text{CF}(\text{CF}_2)_{10}(\text{CH}_2)_2\text{OOCC}=\text{CH}_2$
	$\text{CF}_3 > \text{CF}(\text{CF}_2)_{12}(\text{CH}_2)_2\text{OOCC}=\text{CH}_2$	$\text{CF}_3 > \text{CF}(\text{CF}_2)_4(\text{CH}_2)_3\text{OOCC}=\text{CH}_2$
	$\text{CF}_3 > \text{CF}(\text{CF}_2)_6(\text{CH}_2)_3\text{OOCC}=\text{CH}_2$	$\text{CF}_3 > \text{CF}(\text{CF}_2)_4(\text{CH}_2)_4\text{OOCC}=\text{CH}_2$
	$\text{CF}_3 > \text{CF}(\text{CF}_2)_4(\text{CH}_2)_6\text{OOCC}=\text{CH}_2$	$\text{CF}_3 > \text{CF}(\text{CF}_2)_4(\text{CH}_2)_5\text{OOCCH}=\text{CH}_2$
5	$\text{CF}_3 > \text{CF}(\text{CF}_2)_2(\text{CH}_2)_2\text{OOCCH}_2\text{CH}=\text{CH}_2$	$\text{CF}_3 > \text{CF}(\text{CF}_2)_4(\text{CH}_2)_2\text{OOCCH}_2\text{CH}=\text{CH}_2$
	$\text{CF}_3 > \text{CF}(\text{CF}_2)_6(\text{CH}_2)_2\text{OOCCH}_2\text{CH}=\text{CH}_2$	$\text{CF}_3 > \text{CF}(\text{CF}_2)_7\text{CH}_2\text{OOCCH}_2\text{CH}=\text{CH}_2$
	$\text{CF}_3 > \text{CF}(\text{CF}_2)_{10}(\text{CH}_2)_2\text{OOCCH}_2\text{CH}=\text{CH}_2$	$\text{CF}_3 > \text{CF}(\text{CF}_2)_4(\text{CH}_2)_3\text{OOCCH}_2\text{CH}=\text{CH}_2$
	$\text{CF}_3 > \text{CF}(\text{CF}_2)_4(\text{CH}_2)_3\text{OOCCH}_2\text{CH}=\text{CH}_2$	$\text{CF}_3 > \text{CF}(\text{CF}_2)_6\text{CH}_2\text{OOC}(\text{CH}_2)_2\text{CH}=\text{CH}_2$
	$\text{CF}_3 > \text{CF}(\text{CF}_2)_4(\text{CH}_2)_2\text{OOC}(\text{CH}_2)_5\text{CH}=\text{CH}_2$	$\text{CF}_3 > \text{CF}(\text{CF}_2)_6(\text{CH}_2)_2\text{OOC}(\text{CH}_2)_5\text{CH}=\text{CH}_2$
10	$\text{CF}_3 > \text{CF}(\text{CF}_2)_4(\text{CH}_2)_3\text{OOC}(\text{CH}_2)_5\text{CH}=\text{CH}_2$	$\text{CF}_3 > \text{CF}(\text{CF}_2)_6\text{CH}_2\text{OOCCH}_2\text{CH}=\text{CH}_2$
	$\text{CF}_3 > \text{CF}(\text{CF}_2)_6\text{CH}_2\text{OOCCH}_2\text{CH}=\text{CH}_2$	$\text{CF}_3 > \text{CF}(\text{CF}_2)_6\text{CH}_2\text{OOCCH}=\text{CH}_2$

Group A—5: The compounds belonging to this group are of the formula

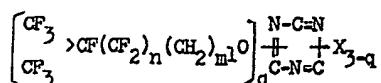


25 wherein  $p^2$  is an integer from 1 to 20, and  $n$  and  $m$  are as defined before:

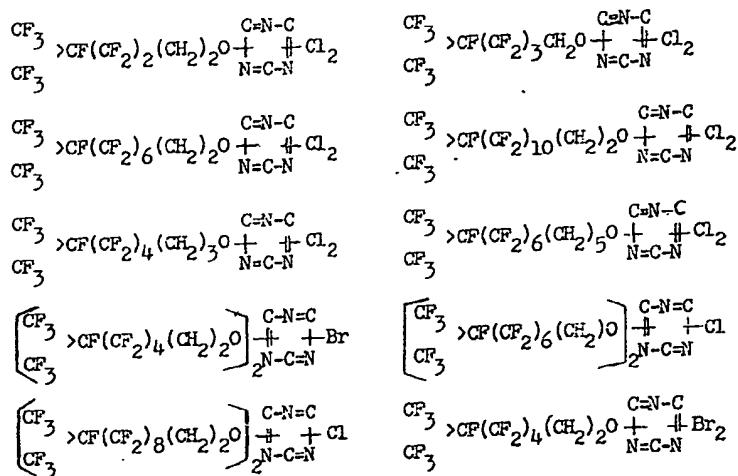
$\text{CF}_3 > \text{CF}(\text{CF}_2)_2\text{COOCH}_2\text{CH}=\text{CH}_2$	$\text{CF}_3 > \text{CF}(\text{CF}_2)_4\text{COOCH}_2\text{CH}=\text{CH}_2$
$\text{CF}_3 > \text{CF}(\text{CF}_2)_6\text{COOCH}_2\text{CH}=\text{CH}_2$	$\text{CF}_3 > \text{CF}(\text{CF}_2)_7\text{COOCH}_2\text{CH}=\text{CH}_2$

	$\text{CF}_3$	$> \text{CF}(\text{CF}_2)_{10}\text{COOCH}_2\text{CH}=\text{CH}_2$	$\text{CF}_3$	$> \text{CF}(\text{CF}_2)_{12}\text{COOCH}_2\text{CH}=\text{CH}_2$
	$\text{CF}_3$		$\text{CF}_3$	
	$\text{CF}_3$	$> \text{CF}(\text{CF}_2)_4(\text{CH}_2)_2\text{COOCH}_2\text{CH}=\text{CH}_2$	$\text{CF}_3$	$> \text{CF}(\text{CF}_2)_5\text{COOCH}_2\text{CH}=\text{CH}_2$
	$\text{CF}_3$		$\text{CF}_3$	
	$\text{CF}_3$	$> \text{CF}(\text{CF}_2)_8(\text{CH}_2)_2\text{COOCH}_2\text{CH}=\text{CH}_2$	$\text{CF}_3$	$> \text{CF}(\text{CF}_2)_4(\text{CH}_2)_5\text{COOCH}_2\text{CH}=\text{CH}_2$
	$\text{CF}_3$		$\text{CF}_3$	
	$\text{CF}_3$	$> \text{CF}(\text{CF}_2)_4(\text{CH}_2)_2\text{COO}(\text{CH}_2)_3\text{CH}=\text{CH}_2$	$\text{CF}_3$	$> \text{CF}(\text{CF}_2)_{14}(\text{CH}_2)_2\text{COOCH}_2\text{CH}=\text{CH}_2$
	$\text{CF}_3$		$\text{CF}_3$	
5	$\text{CF}_3$	$> \text{CF}(\text{CF}_2)_6(\text{CH}_2)_2\text{COOCH}_2\text{CH}=\text{CH}_2$	$\text{CF}_3$	
	$\text{CF}_3$		$\text{CF}_3$	

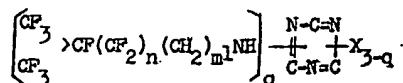
10 *Group A—6:* The compounds belonging to this group are of the formula



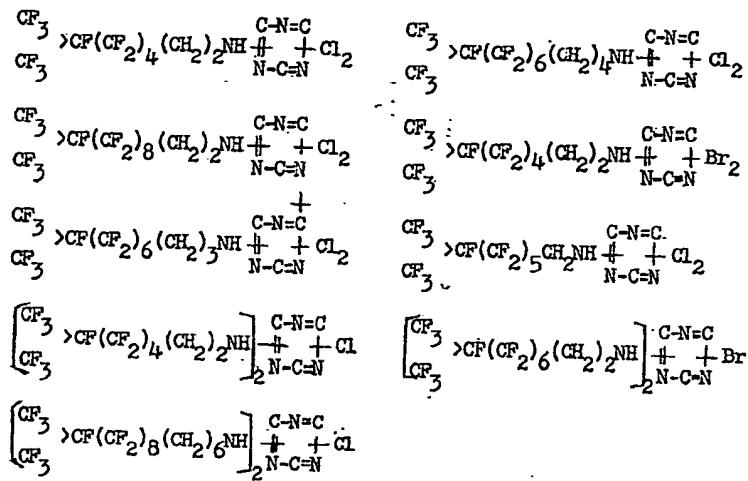
wherein  $q$  is 1 or 2; and  $X$  and  $m^1$  are as defined before:



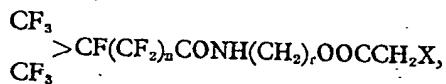
*Group A—7:* The compounds belonging to this group are the formula



wherein  $n$ ,  $m^1$ ,  $q$  and  $X$  are as defined before:



*Group A—8:* The compounds belonging to this group are of the formula

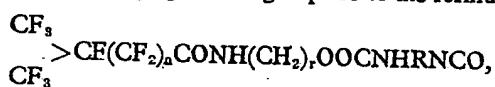


wherein  $r$  is an integer from 2 to 10, and  $n$  and  $X$  are as defined before:

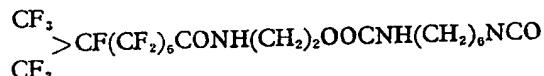
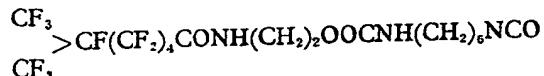
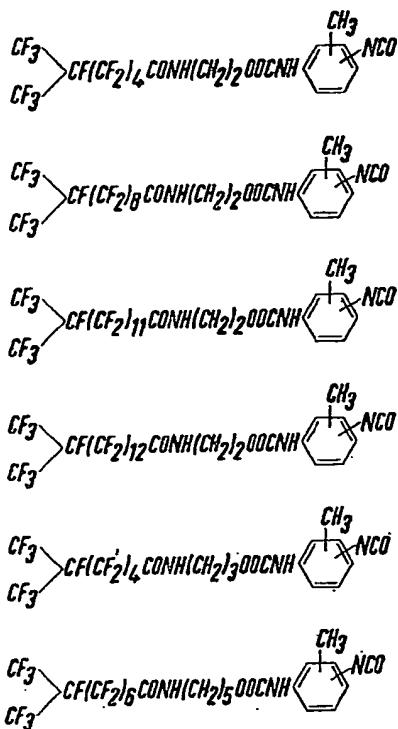
5	$\text{CF}_3$ $\text{CF}_3 > \text{CF}(\text{CF}_2)_4 \text{CONH}(\text{CH}_2)_2 \text{OOCCH}_2 \text{Cl}$	$\text{CF}_3$ $\text{CF}_3 > \text{CF}(\text{CF}_2)_6 \text{CONH}(\text{CH}_2)_2 \text{OOCCH}_2 \text{Br}$
	$\text{CF}_3$ $\text{CF}_3 > \text{CF}(\text{CF}_2)_8 \text{CONH}(\text{CH}_2)_2 \text{OOCCH}_2 \text{Cl}$	$\text{CF}_3$ $\text{CF}_3 > \text{CF}(\text{CF}_2)_{11} \text{CONH}(\text{CH}_2)_2 \text{OOCCH}_2 \text{Cl}$
	$\text{CF}_3$ $\text{CF}_3 > \text{CF}(\text{CF}_2)_6 \text{CONH}(\text{CH}_2)_5 \text{OOCCH}_2 \text{Cl}$	$\text{CF}_3$ $\text{CF}_3 > \text{CF}(\text{CF}_2)_4 \text{CONH}(\text{CH}_2)_4 \text{OOCCH}_2 \text{Br}$

10

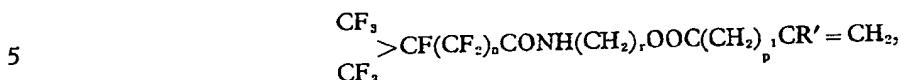
*Group A—9:* The compounds belonging to this group are of the formula



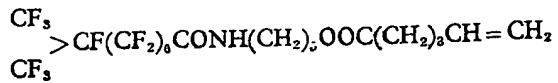
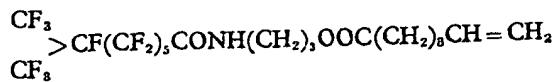
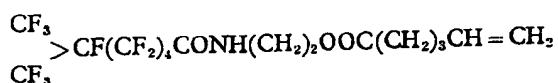
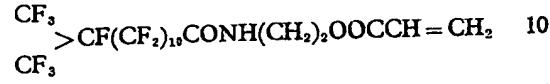
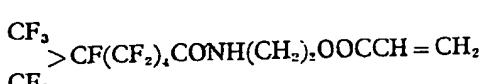
wherein  $n$ ,  $r$  and  $R$  are as defined before:

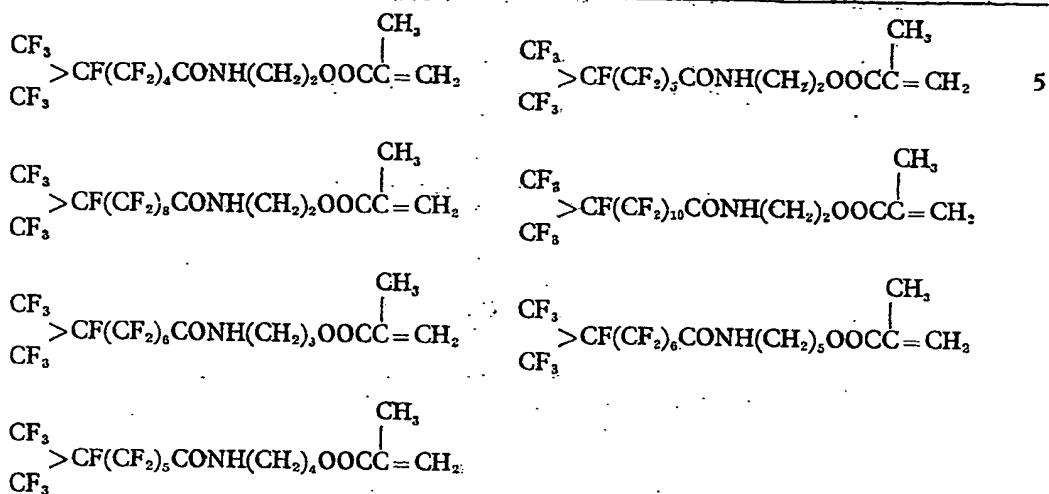


*Group A—10:* The compounds belonging to this group are of the formula

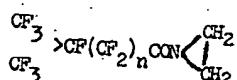


wherein  $n$ ,  $r$ ,  $p$ ' and  $\text{R}'$  are as defined before:

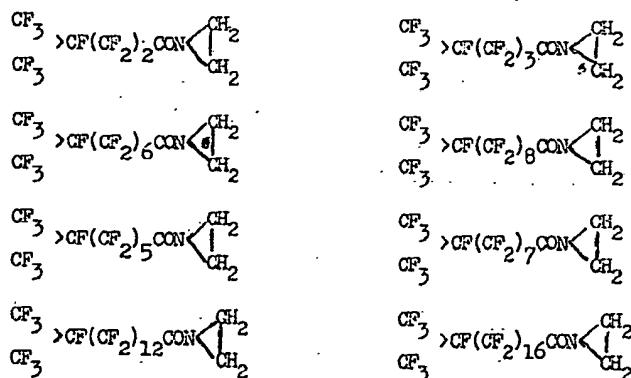




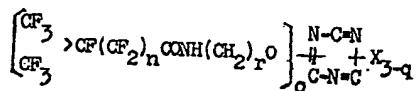
*Group A-11:* The compounds belonging to this group are of the formula



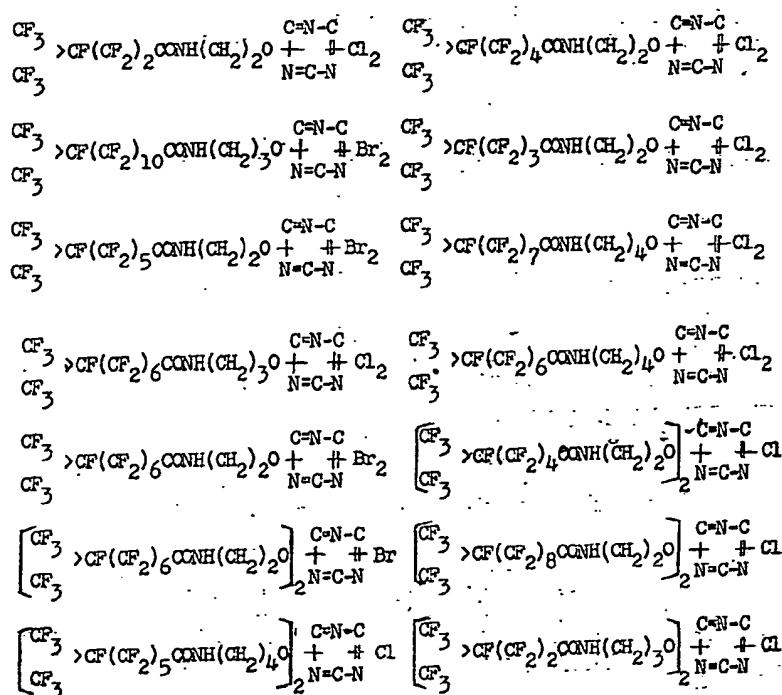
10 wherein n is as defined before.



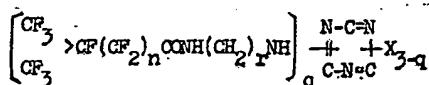
*Group A-12:* The compounds belonging to this group are of the formula



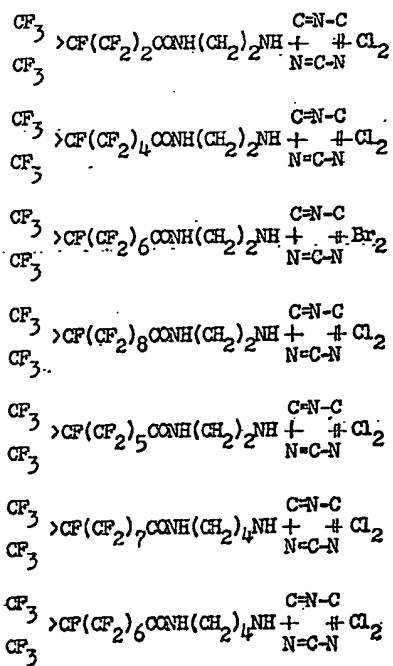
wherein X, n, r and q are as defined before:

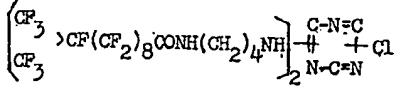
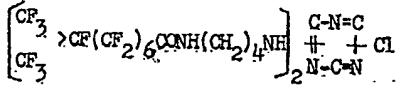
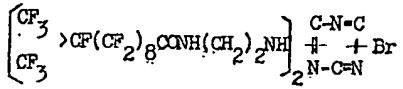
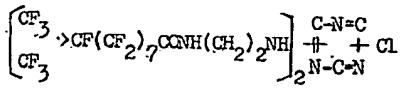
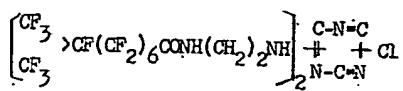
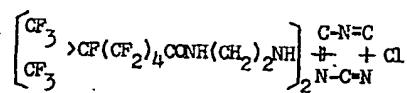


Group A-13: The compounds belonging to this group are of the formula



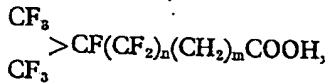
wherein X, n, q and r are as defined before:





**Group B:** The compounds belonging to this group consist of chromium, zirconium, aluminum and iron salts of fluoroalkyl-containing carboxylic acids of the formula

5



n and m being as defined before. The chemical structure of said salts are not necessarily clear, but the salts may be understood as belonging to the multi-nuclear or complex salts. By the term 'salt' employed in association with the compounds of Group B throughout the specification and claims are accordingly meant not only multi-nuclear salts but complex salts.

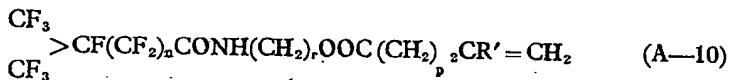
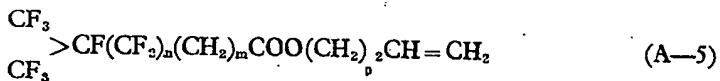
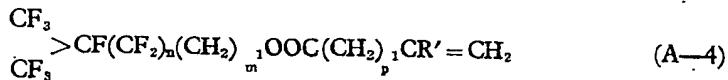
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15

**Group C:** The compounds belonging to this group consist of:

(a) Polymers of the fluorine-containing unsaturated compounds belonging to Groups A-4, A-5 and A-10, namely of the formulae:

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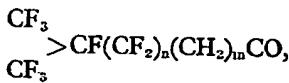


25 wherein R', n, m, m<sup>1</sup>, p<sup>1</sup>, p<sup>2</sup> and r are as defined before:

(b) Copolymers of at least two compounds respectively belonging to any of the aforesaid formulas A-4, A-5 and A-10;

30 (c) Copolymers of at least one compound belonging to any of the aforesaid formulas A-4, A-5 and A-10 and any of the other polymerizable monomers of other kinds having at least one ethylene linkage; and

35 (d) Certain polyesters obtained by esterifying polyvinyl alcohols with a fluoroalkyl-containing carboxylic acid halide of the formula

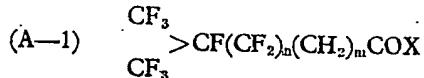


wherein m, n and X are as defined before.

40 All the branched-chain fluorine-containing compounds belonging to aforesaid Groups A to C are manufactured in the manners, the representative instances of which are as follows:

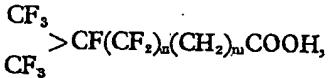
#### SYNTHESIS OF GROUP A COMPOUNDS

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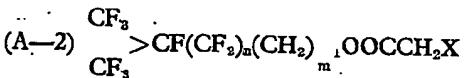
The compounds belonging to this formula are synthesized by reacting a fluoroalkyl-containing carboxylic acid of the formula

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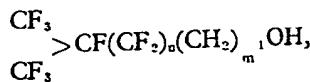


n and m being as defined before, or an alkali metal salt thereof with a phosphorus pentahalide, phosphorus trihalide or thionyl halide at a temperature ranging from normal room temperature to the reflux temperature.

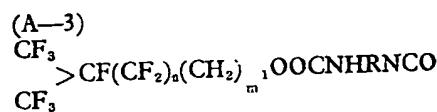
55



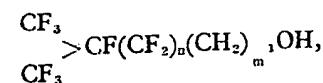
The compounds belonging to this formula are produced by reacting a fluoroalkyl-containing alcohol of the formula



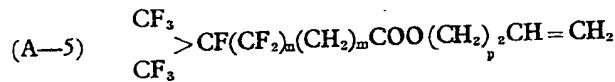
5 n and m<sup>1</sup> being as defined before, with a monohaloacetyl halide at a temperature from about 100° to about 150° C.



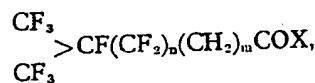
20 The compounds belonging to this formula are synthesized by reacting a fluoroalkyl-containing alcohol of the formula



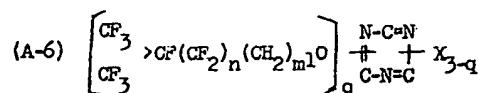
25 n and m<sup>1</sup> being as defined before, with an unsaturated aliphatic carboxylic acid of the formula



40 The compounds belonging to this formula are manufactured by esterifying a compound belonging to Group A-1, namely a compound of the formula

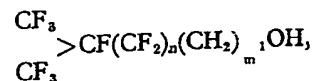


45 n, m and X being as defined before, with an unsaturated aliphatic alcohol of the formula  $\text{CH}_2=\text{CH}(\text{CH}_2)_{p-1}\text{OH}$ , p<sup>2</sup> being as defined before, at the reflux temperature.



The compounds belonging to this formula are synthesized by reacting alkali alcoholate of the formula

The compounds belonging to this formula are manufactured by reacting in the presence of toluene a fluoroalkyl-containing alcohol of the formula

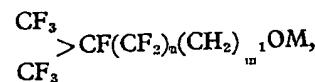


n and m<sup>1</sup> being as defined before, with excess diisocyanate of the formula  $\text{OCNRNC}\bar{\text{O}}$ , R being as defined before, at the reflux temperature.

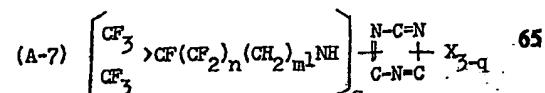


R' and p<sup>1</sup> being as defined before, or with an acid halide thereof at the reflux temperature. The reaction is usually carried out in a liquid medium, such as carbon tetrachloride or toluene. There are desirably added a dehydrating agent, such as concentrated sulfuric acid or a hydrogen halide acceptor, such as pyridine, and a polymerization inhibitor, such as copper powder or hydroquinone.

30 35



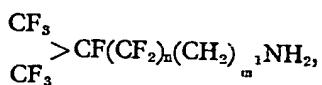
50 M being an alkali metal, and n and m<sup>1</sup> being as defined before, with a cyanuric halide in a cooling medium consisting of acetone dissolved in aqueous media in the order of from 2 to 8 parts by volume on the basis of said aqueous media at a pH adjusted to 6 to 7 with a 10 weight percent sodium carbonate aqueous solution. The value of q of the resultant compounds varies in accordance with the composition ratio of the starting stock. The resultant products usually contain the compounds in which q is 1 and 2, which compounds, however, are not necessarily to be separated.



55 60

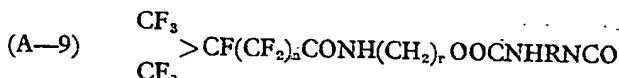
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The compounds belonging to this formula are produced by reacting a fluorine-containing alkylamine of the formula

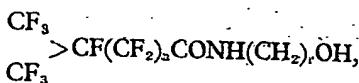


5 n and m<sup>1</sup> being as defined before, with a cyanuric halide under the same reaction conditions as employed for the synthesis of Group A—6 compounds.

(A—8)

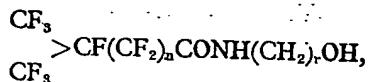


20 The compounds belonging to this formula are synthesized by reacting a fluoroalkyl-containing alcohol of the formula



n and r being as defined before, with excess diisocyanate of the formula OCNRNCO, R A—3 compounds.

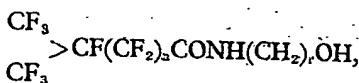
The compounds belonging to this formula are manufactured by reacting a fluoroalkyl-containing alcohol of the formula



n and r being as defined before, with a mono-haloacetyl halide under the same conditions as employed for the synthesis of Group A—2 compounds.

15

20 The compounds belonging to this formula are synthesized by reacting a fluoroalkyl-containing alcohol of the formula

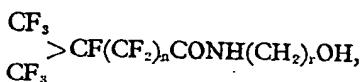


n and r being as defined before, under the same conditions as employed for the synthesis of Group A—3 compounds.

25

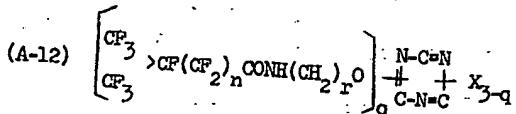


30 The compounds belonging to this formula are prepared by reacting a fluoroalkyl-containing alcohol of the formula

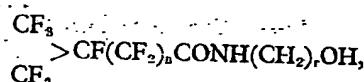


n being as described before, with ethylene imine in an equimolar ratio or thereabout. The crude products are fractionally distilled to expel the fractions of lower boiling points and evaporated to dryness.

50

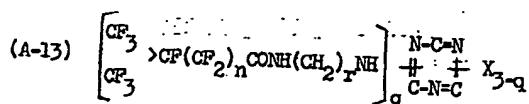


The compounds belonging to this formula are produced by reacting an alkali alcoholate of an alcohol of the formula

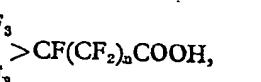


55

n and r being as defined before, with a cyanuric halide under the same reaction conditions as employed for the synthesis of Group A—6 compounds.

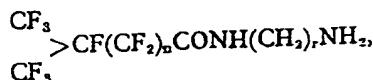


40 The compounds belonging to this formula are obtained by reacting in a solvent, such as ether, at a temperature below 0° C. an alkyl ester or an acid halide of a carboxylic acid of the formula



45

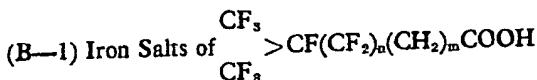
The compounds belonging to this formula are synthesized by reacting a compound of the formula



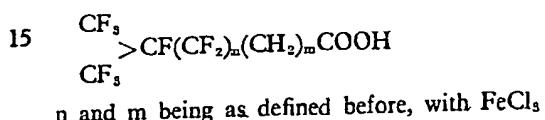
n and r being as defined before, with a cyanuric halide under the same reaction conditions for the synthesis of Group A-7 compounds.

### SYNTHESIS OF GROUP B COMPOUNDS

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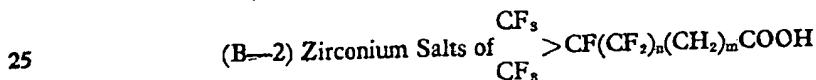


The compounds belonging to this group are manufactured by reacting a carboxylic acid of the formula

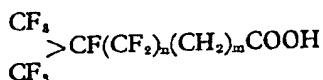


in aqueous media at a temperature from normal room temperature to about 50° C. The molecular weight and solubility of the resultant products vary in accordance with the composition ratio of the starting stock. There are desirably employed  $\text{FeCl}_3$  in the order of from 0.5 to 1 mole per 1 to 0.5 mole of said carboxylic acid.

20

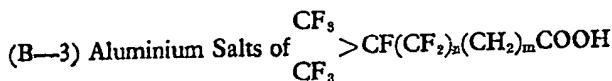


The compounds belonging to this group are synthesized by reacting an alkali metal salt of the carboxylic acids of the formula

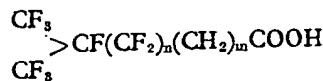


n and m being as defined before, with zirconium chloride or zirconium oxychloride in the same composition ratio and under the same reaction conditions as employed for the synthesis of Group B-1 compounds. The molecular weight and solubility of the resultant products vary in accordance with the composition ratio of the starting stock.

35



The compounds belonging to this group are obtained by reacting in aqueous media a carboxylic acid of the formula

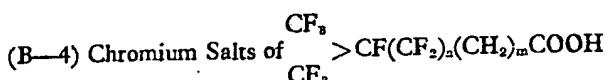


n and m being as defined before, with aluminum chloride under the same reaction

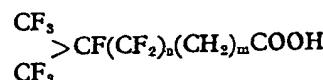
conditions as employed for the production of Group B-1 compounds. Alternatively, said carboxylic acid is reacted with stirring at a temperature from about 50° to about 100° C. with aluminum powder in the presence of a little  $\text{HgCl}_2$  in a  $\text{C}_1$  to  $\text{C}_8$  aliphatic alcohol. The molecular weight and solubility of the resultant products vary in accordance with the composition ratio of the starting stock.

45

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The compounds belonging to this group are manufactured by reducing a  $\text{C}_1$  to  $\text{C}_3$  aliphatic alcohol with  $\text{CrO}_3$  in the presence of a carboxylic acid of the formula



n and m being as defined before. Alternatively, said carboxylic acid is reacted with chromyl chloride in the presence of a reducing agent, such as methanol, in an organic solvent. The molecular weight and solubility of the resultant products vary in accordance with the composition ratio of the starting stock.

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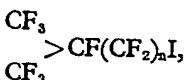
SYNTHESIS OF STARTING  
MATERIALS FOR GROUP A AND B  
COMPOUNDS

5 The starting materials for the production of the compounds belonging to Groups A and B can be manufactured by various methods, of which the following are illustrative instances employed in this invention:

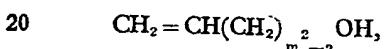
*Method 1: Synthesis of*



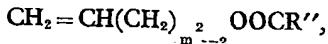
The fluoroalkyl-containing alcohols of this formula to be employed for the production of the compounds belonging to Groups A-2, A-3, A-4 and A-6 are manufactured by 40  
15 the addition reaction of a compound of the formula



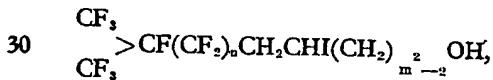
n being as defined before, with a compound of the formula



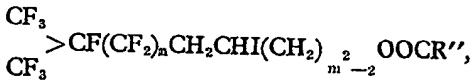
$m^2$  being an integer from 3 to 20, or of the formula



25 wherein  $\text{R}''$  is a  $\text{C}_1$  to  $\text{C}_8$  alkyl group and  $m^2$  is as defined before, in the presence of a free radical initiator, such as an organic peroxide or azo compound, and then by reducing the resultant products, when said products are of the formula

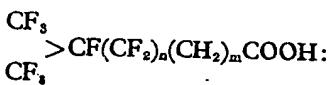


n and  $m^2$  being as defined before, or by reducing and hydrolyzing the products, when said products are of the formula



35 n,  $m^2$  and  $\text{R}''$  being as defined before.

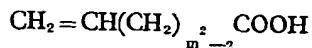
*Method 2: Synthesis of*



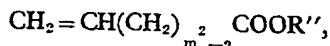
The fluoroalkyl-containing carboxylic acids of this formula to be employed for the production of the compounds belonging to Groups A-1, A-5, A-8 to A-13 and B are prepared by the addition reaction of a compound of the formula 40



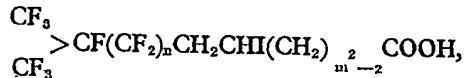
n being as defined before, with



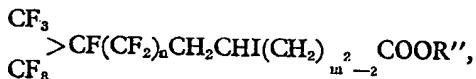
or



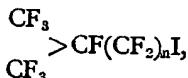
$m^2$  and  $\text{R}''$  being as defined before, in the presence of a free radical initiator, such as an organic peroxide or organic azo compound. Then the resultant compounds of the formula 50



n and  $m^2$  being as defined before, are reduced and the compounds of the formula

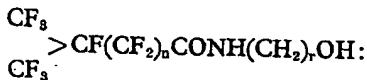


wherein n,  $m^2$  and  $\text{R}''$  are as defined above, are reduced and hydrolyzed, to produce the desired compounds. Alternatively, said fluoroalkyl-containing carboxylic acids can be prepared by reacting a compound of the formula 60

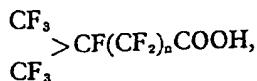


n being as defined before, with  $\text{CH}=\text{CH}$  or with a compound of the formula  $\text{CH}_2 = \text{CHA}$  or  $\text{CF}_2 = \text{CX}_2$ , A being a halogen,  $-\text{OR}''$ ,  $-\text{OOCR}''$ ,  $-\text{COOR}''$  or  $-\text{COOH}$ ,  $\text{R}''$  being as defined before, and X being as defined before and both X'es are mutually exclusive in case of F and dehydroiodination and oxidization of the resultant products, said dehydroiodination being unnecessary where  $\text{CF}_2 = \text{CX}_2$  is employed. This method was accomplished by the present inventors and is disclosed and claimed in U.K. Patent Application No. 5130/65 Serial No. 1,092,141. 65

*Method 3: Synthesis of*

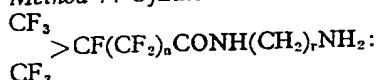


5 The compounds of this formula to be employed for the production of the compounds belonging to Groups A—8, A—9, A—10 and A—12 are prepared by reacting an aminoalcohol having the formula  $H_2N(CH_2)_rOH$  in ether at a temperature from about  $5^\circ$  to  $10^\circ$  C. with an alkyl ester of an carboxylic acid of the formula

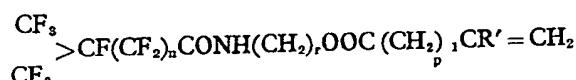
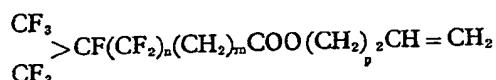
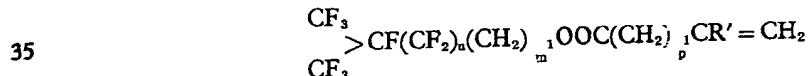


10 n being as defined before, prepared in accordance with Method 2.

Method 4: Synthesis of



15 The compounds of this formula to be employed for the production of the compounds belonging to Group A—13 are manufactured by re-



wherein n, m<sup>1</sup>, p<sup>1</sup>, m, p<sup>2</sup>, r and R' are as defined before; copolymers of at least 2 of the 40 compounds respectively belonging to said formulae; and copolymers of at least one of the compounds belonging to said formulae and a copolymerizable substance:

45 For the production of said homopolymers and copolymers, there can be employed under any suitable condition any suitable method, such as bulk polymerization, solution polymerization, suspension polymerization, emulsion polymerization, irradiation polymerization or photochemical polymerization, of which the most general is emulsion polymerization, namely, a conventional method employed for the emulsion polymerization of vinyl compounds. For instance, one or more monomers 50 are emulsified in aqueous media in the presence of a surface active agent to produce a desired compound. There is added, where necessary, a free radical initiator, such as an organic peroxide.

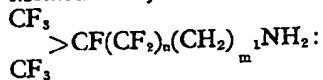
55 The polymerizable substances which are employed in conjunction with the unsaturated compounds of said formulae include (a) acrylates and methacrylates, such as methyl-,

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acting a 28 percent ammonia water at a temperature from about  $120^\circ$  to about  $180^\circ$  C. under autogenous pressure with a perfluoroalkyl-containing alcohol prepared in accordance with Method 3.

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Method 5: Synthesis of



The compounds of this formula to be employed for the production of the compounds belonging to Group A—7 are manufactured by reacting concentrated ammonia water at a temperature from about  $120^\circ$  to  $180^\circ$  C. under the autogenous pressure with a fluorine-containing alcohol prepared in accordance with Method 1.

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SYNTHESIS OF GROUP C COMPOUNDS

(C—1) Synthesis of homopolymers of the compounds of the formulae:

65 ethyl-, butyl-, isobutyl-, propyl-, 2-ethylhexyl-, hexyl-, decyl-, lauryl- and stearyl-acrylate and methacrylate; (b) vinyl esters of aliphatic acids, such as acetic acid, propionic acid, caprylic acid, laurylic acid and stearic acid; (c) styrene,  $\alpha$ -methylstyrene, p-methylstyrene, and the like styrene compounds; (d) vinyl fluoride, vinyl chloride, vinyl bromide, vinylidene fluoride, vinylidene chloride and the like halogenated vinyl and vinylidene compounds; (e) allyl carboxylates, such as allyl acetate, allyl propionate, allyl caproate, and allyl stearate; (f) vinyl methyl ketone, vinyl ethyl ketone and the like vinyl alkyl ketones; (g) N-methyl acrylamide, N-methyl methacrylamide, glycidyl acrylate, glycidyl methacrylate, and the like acrylamides; and (h) 2,3-dichloro-1,3-butadiene, isoprene, and the like butadienes.

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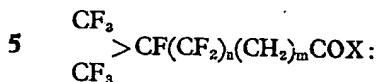
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85 Any of the fluorine-containing monomers of this invention can be copolymerized with any of said polymerizable substances in a wide range of polymerization ratio. In order to obtain the most effective water-repellency and oil-repellency, however, there should be employed the starting fluorine-containing

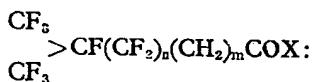
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monomers in the order of at least 25 percent by weight.

(C-2) Synthesis of polyesters of polyvinyl alcohols and



The polyvinyl alcohols employed in this invention are of an average polymerization degree of from 300 to 1,000 and a saponification value of from 70 to 100 percent. Such polyvinyl alcohols are esterified with an acid halide of the formula



15                     $n, m$  and  $X$  being as defined before, in dimethyl formamide in the presence of pyridine or the like hydrogen halide acceptor at a temperature from about 50° C. to the reflux temperature. The esterification value and solubility of the resultant products are dependent upon the composition ratio of the starting polyvinyl alcohol and acid halide. The acid halide is normally employed in the order of from 0.3 to 1 mole per mole of the hydroxyl group of the starting polyvinyl alcohol, and the esterification of the hydroxyl group 20 of the polyvinyl alcohol is profitably carried out within the range of 30 to 100 percent.

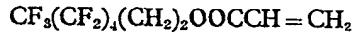
25                    The water-repellent and oil-repellent compositions of this invention comprise any of the branched-chain fluorine-containing compounds belonging to said Groups A to C dissolved or suspended in a liquid medium. For a sufficient water-repellency and oil-repellency, there is employed any of said compounds in an amount of at least 0:1 gram per 100 milliliter with the upper limit selected from a wide range of concentration. From the economic points of view, however, suitable order of concentration is below 20 grams per 100 milliliters, preferably from 1 to 10 30 grams per 100 milliliters, for the compounds belonging to Group A, and below 10 grams per 100 milliliters, preferably from 0.5 to 5 grams per 100 milliliters for the compounds belonging to Groups B and C.

35                    The water-repellent and oil-repellent compositions comprising any of the compounds belonging to Group A may be employed in the form of a solution. As a solvent, there may be employed toluene, acetone, ether, dimethylformamide or trichlorofluoroethane selected in accordance with the properties of the compounds to be dissolved.

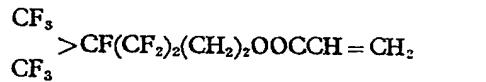
40                    The water-repellent and oil-repellent compositions comprising any of the compounds belonging to Group B may also be employed in the form of a solution. The solvents to be employed should be determined in view of the

45                    properties of the compound to be dissolve, but there may profitably be employed a  $\text{C}_1$  to  $\text{C}_3$  aliphatic alcohol or trichlorotrifluoroethane. Of the chromates belonging to Group B-4, the compounds prepared with chromyl chloride are profitably water-soluble.

50                    The water-repellent and oil-repellent compositions comprising any of the compounds belonging to Group C may be employed in the form of either suspension or solution. When employed in the form of a suspension, the aqueous suspension prepared by emulsion polymerization is employed in the original state or by suitably diluting or concentrating. When employed in the form of a solution, any of the compounds belonging to Group C is dissolved in a solvent, such as not only trichlorotrifluoroethane and the like fluorine-containing solvents but acetone, ether and the like conventional organic solvents. The compounds of this invention have a wider range of solubility because of the branched-chain fluoroalkyl group bonded to the end position than any similar compound having a straight-chain fluoroalkyl group. For instance, polymers derived by emulsion polymerization from



60                    require a long period of time with stirring before being completely dissolved in trichlorotrifluoroethane or the like fluorine-containing solvents, whereas polymers derived by emulsion polymerization from



70                    having the same number of carbon atoms are not only easily soluble in trifluorotrichloroethane but fairly soluble in acetone, ether and the like conventional organic solvents. Such being the case, there is no need of employing such emulsifying agents as having bad effects on the water-repellency and oil-repellency of the resultant compositions.

#### MODES OF APPLICATION

75                    The water-repellent and oil-repellent compositions of this invention can be applied in various modes in accordance with the species of the compounds of this invention employed as an effective ingredient. Hereinafter are described some instances of said application, which are illustrative only and not limiting the scope and extent of this invention.

80                    1. APPLICATION OF GROUP A COMPOUND-CONTAINING COMPOSITIONS: As stated before, the compounds of this invention belonging to Group A have a branched-chain fluoroalkyl group bonded to one end position and a group attached to the other end position, said atomic group having an ability to form a chemical bond with a hydroxyl, carboxyl or an amino

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group, so that the articles to be treated therewith include those articles having hydroxyl, carboxyl, or amino groups, which can easily form a chemical bond with said atomic group, 5 whereby there are produced a high order of water-repellency and oil-repellency together with an improved durability against washing, cleaning and wearing. Conditions for the application of said compounds vary in accordance with the species of the compounds to be 10 employed as an effective ingredient.

(a) *Application of Group A—1, A—2, A—6, A—7, A—8, A—12 and A—13 compound-containing compositions:* The compositions 15 comprising any of the compounds belonging to Groups A—1, A—2, A—6, A—7, A—8, A—12 and A—13 are employed in the form of a solution prepared in accordance with the manners as described before. There may be 20 added, where necessary, pyridine, sodium carbonate or the like hydrogen halide acceptor. The article to be treated is dipped in the solution, and the reaction is carried out at a temperature ranging from normal room temperature to about 80° C. for about 10 to 30 25 minutes either while dipping or after squeezing, whereby the compound of this invention employed is allowed to form a chemical bond with the —O— bond of the hydroxyl group of 30 the article being treated. The articles to be treated in such manners include cellulose, polyvinyl alcohols and other hydroxyl group-containing materials, particularly, fibres, yarns, fabrics, unwoven fabrics, papers, films, fibre 35 plates, and the like fibrous and porous fabricates.

(b) *Application of Group A—3 and A—9 compound-containing compositions:* The water-repellent and oil-repellent compositions 40 comprising any of the compounds belonging to Groups A—3 and A—9 are employed in the form of a solution prepared in accordance with the manners as described before. The article to be treated is dipped in said 45 solution, and the reaction is carried out at a temperature ranging from about 80° to about 150° C. for about 5 to 30 minutes either while dipping or after squeezing, whereby said compound is allowed to form a chemical bond 50 with the —O— bond of the hydroxyl group or with the —NH— bond of the amino group of the article being treated. The articles to be treated in such manners include cellulose, polyvinyl alcohols, polyamides and other 55 hydroxyl group- or amino group-containing materials, particularly, fibres, yarns, fabrics, unwoven fabrics, papers, films, fibre plates, and the like fibrous and porous fabricates.

(c) *Application of Group A—11 compound-containing compositions:* The water-repellent and oil-repellent compositions comprising any 60 of the compounds belonging to Group A—11 are employed in the form of a solution prepared in accordance with the manners as described before. The article to be treated is

dipped in said solution, and the reaction is carried out at a temperature from about 80° to about 150° C. for about from 5 to 30 minutes either while dipping or after squeezing, whereby said compound is allowed to 70 form a chemical bond in the form of a



bond with the carboxyl group of the article being treated. The articles to be treated in such manners include wool and other carboxyl group-containing materials, particularly, fibres, yarns, fabrics, unwoven fabrics, papers, films, fibre plates, and the like fibrous and porous fabricates.

(d) *Application of Group A—4, A—5 and A—10 compound-containing compositions:* The water-repellent and oil-repellent compositions comprising any of the compounds belonging to Groups A—4, A—5 and A—10 are employed in the form of a solution. The article to be treated is mercerized with alkali hydroxide if necessary, and then dipped in the solution prepared in the manners as described before. The reaction is carried out at a temperature ranging from normal room temperature to the reflux temperature under irradiation of ultraviolet rays for about from 0.5 to 30 hours either while dipping or after squeezing, whereby the —CR'=CH<sub>2</sub> group, R' being as defined before, of the compound employed is allowed to form a chemical bond with the —OH of the article being treated. The articles to be treated in such manners include cellulose, polyvinyl alcohols and other hydroxyl group-containing materials, particularly, fibres, yarns, fabrics, unwoven fabrics, papers, films, fibre plates, and the like fibrous and porous fabricates.

2. **APPLICATION OF GROUP B COMPOUND-CONTAINING COMPOSITIONS:** Unlike Group A compound-containing compositions, the water-repellent and oil-repellent compositions comprising any of the compounds belonging to Group B form a coating onto the article being treated without forming a chemical bond, so that the articles to be treated therewith include a wide variety of solid type. The compositions comprising any of said compounds of Group B are employed in the form of a solution prepared in accordance with the manners as described before, and impregnated in or coated onto the article being treated by dipping, spraying or padding. The resultant article is allowed to dry at room temperature or heat cured. Particularly, the articles treated with the composition comprising a chromium salt derived from chromyl chloride is cured at a temperature of from 80° to 150° C. or thereabout for about from 1 to 30 minutes. Said chromium salt compositions further have a wide range of application, because the compositions are obtained in the form of an aqueous solution. When the article being

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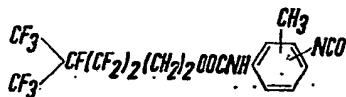
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treated has a hydroxyl group, the chromium salt composition supposedly forms a co-ordinated bond therewith.

3. APPLICATION OF GROUP C COMPOUND-  
CONTAINING COMPOSITIONS: The water-repellent and oil-repellent compositions comprising any of the compounds belonging to Group C also do not form a chemical bond with the articles being treated, so that the articles to be treated therewith include a wide variety of solid type. Said composition is employed in the form of solution or suspension, and impregnated in or coated onto the article being treated by dipping, spraying or padding. The resultant article is allowed to dry at room temperature. In the case of the composition employed in the form of a suspension, the dried article is preferably heat-treated at a temperature from 80° to 180° C. or thereabout for about from 1 to 30 minutes to make continuous the polymer particles attached onto the article or to cause the particles firmly adhered to the article. For a higher order of durability said heat-treatment is also desirably applied to those articles treated with the composition employed in the form of a solution. The emulsifying or suspending agents employed and which have a bad effect on the resultant water-repellency and oil-repellency are washed off by soaping during or after the heat-treatment.

All of the water-repellent and oil-repellent compositions of this invention impart a markedly high order of water-repellency and oil-repellency to the articles treated therewith. Such working effect may be clearly understood when compared with the compositions comprising a compound having a straight-chain fluoroalkyl group of the formula  $CF_3(CF_2)_c-$ , c being as defined before.

For instance, the cotton gauze impregnated to the order of 0.5 percent by weight by dry pickup with



45 of this invention displayed an ability to completely block the infiltration of a 50:50 by volume mixture of n-heptane and liquid paraffin more than 3 hours, whereas the control gauze similarly impregnated to the order of from 0.5 to 0.6 percent by weight of dry pickup with



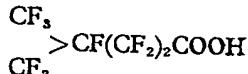
55 failed to hold a 50:50 by volume mixture of n-heptane and liquid paraffin, although said article obstructed the passage of a 40:60 by volume mixture of n-heptane and liquid

paraffin, and another control gauze impregnated to said order with



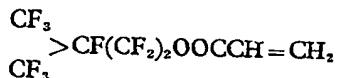
60 having the same chain length as the aforesaid branched-chain compound of this invention could not sustain even a 40:60 by volume mixture of n-heptane and liquid paraffin.

65 Further, the cotton gauze treated with a chromium salt of

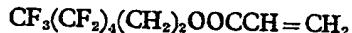


70 of this invention dissolved in the order of 0.1 percent by weight per volume in isopropanol sustained machine oil and liquid paraffin for more than 24 hours, whereas the control gauze treated in the same order with a chromium salt of  $CF_3(CF_2)_4COOH$  having a longer chain than but the same number of carbon atoms as the aforesaid branched-chain compound of this invention could not hold machine oil and liquid paraffin even for 10 minutes.

75 Still further, the cotton gauze impregnated to the order of 0.5 percent by weight by dry pickup with a 0.2 percent by weight aqueous emulsion of a polymer of



80 of this invention completely held liquid paraffin for 3 days, displaying an ability to block the infiltration of a 40:60 by volume mixture of liquid paraffin and n-heptane, whereas the control article impregnated in the same manner with a 0.2 percent aqueous emulsion of a polymer of



85 held liquid paraffin only for 24 hours and failed to sustain a 40:60 mixture by volume of liquid paraffin and n-heptane.

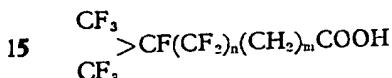
90 Such outstanding effects of the compositions of this invention are supposedly due to the presence of a branched-chain fluoroalkyl group of the formula



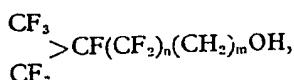
95 n being as defined before, bonded to the end position of the compounds of this invention, but the theoretical ground of the fact that the branched-chain fluoroalkyl-containing compounds of this invention display a particularly

pronounced water-repellency and oil-repellency as compared with the corresponding straight-chain fluoroalkyl-containing compounds is not necessarily clear. It may however be safely 5 added that the composition prepared from the compounds having said branched-chain fluoroalkyl group display a high order of  $\text{CF}_3-$  concentration, so that the resultant contact angle with water becomes larger than that of 10 the compounds having a straight-chain fluoroalkyl group.

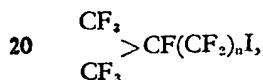
For a fuller understanding of the principles of this invention, there are described herein-after preferred methods for the production of



and

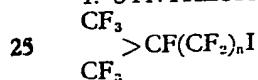


*n* and *m* being as defined before, and the manufacture of

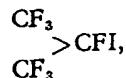


*n* being as defined before, to be employed for preparing the compounds of the aforesaid formulae.

#### 1. SYNTHESIS OF

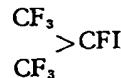


In a 500-cc Hastelloy-C agitator-type autoclave, Hastelloy-C being a Trade Mark of Union Carbide Corporation, U.S.A., were placed 185 grams (0.625 mole) of perfluoro-30 isopropyl iodide of the formula



0.7 gram of tertiarybutylhydroperoxide, and 3.3 grams of ditertiarybutylperoxide. After freezing the mixture with liquid nitrogen and evacuating the air in the autoclave, there were added 35.0 grams (0.350 mole) of tetrafluoroethylene, and the mixture was steam-heated with stirring. The reaction temperature rose to 100.5° C. and the pressure to 40 20.5 kg/cm<sup>2</sup>.g. at the highest 10 minutes after application of steam. The pressure however started to fall thereafter. When the pressure fell to 6 kg/cm<sup>2</sup>.g. 5 hours after application of steam, stirring was suspended and 45 the mixture was cooled with water. The pres-

sure reached almost 0 kg/cm<sup>2</sup>.g. Fractional distillation of the resultant products obtained in an amount of 217 grams produced 139.6 grams (0.472 mole) of the unreacted  $\text{CF}_3\text{CFICF}_3$ , 20.9 grams (0.0528 mole) of the monomolar addition product of  $\text{CF}_2=\text{CF}_2$ , 25.3 grams (0.0510 mole) of the dimolar addition product of  $\text{CF}_2=\text{CF}_2$ , 13.1 grams (0.0264 mole) of the trimolar addition product of  $\text{CF}_2=\text{CF}_2$ , 10.5 grams (0.0176 mole) of the tetramolar addition product of  $\text{CF}_2=\text{CF}_2$ , and 4.2 grams of the pentamolar and more molar addition products of  $\text{CF}_2=\text{CF}_2$ . Conversion for



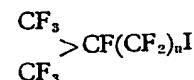
and  $\text{CF}_2=\text{CF}_2$  is respectively 24.5 and 96.1 percent.

The compounds in which *n* is an odd integer can be prepared by various methods.

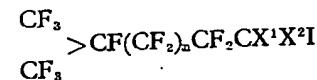
For example, the starting fluoroalkyl-containing carboxylic acids having the formula



(wherein *u* is an even integer) can be prepared by reacting perfluoro iodide



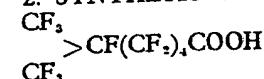
with  $\text{CF}_2=\text{CX}^1\text{X}^2$  (wherein  $\text{X}^1$  and  $\text{X}^2$  being respectively —H, —F, —Cl, —Br or —I, said  $\text{X}^1$  and  $\text{X}^2$  being mutually exclusive in terms of —F), oxidizing the resultant adducts



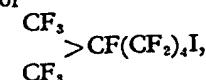
with fuming sulfuric acid or oxygen, and hydrolyzing the resultant acid halide.

This process is illustrated in our co-pending Application No. 5130/65 Serial No. 1,092,141 (especially in Examples 4 and 8).

#### 2. SYNTHESIS OF

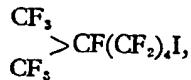


In a 150-cc Hastelloy-C agitator-type autoclave were placed 150 grams (0.303 mole) of



7 grams (0.250 mole) of ethylene, and 1

gram of azobisisobutyronitrile. After completely evacuating the air, the mixture was agitated at 60° to 70°C. for 5 hours. 2.5 Grams of the ethylene were then removed, and the liquid product was fractionally distilled, producing 79.3 grams of the unreacted



69.3 grams of a crude addition product of the formula



and 5.9 grams of other fractions.

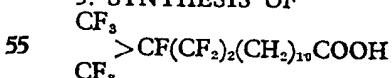
There were placed on the other hand in a 100-cc four-neck flask 18 grams of KOH and 20 grams of ethanol and stirred. To the resultant homogeneous mixture were added slowly 63 grams of said



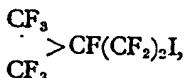
A violent exothermic reaction took place which was cooled with water, and the reaction was carried out at 50° to 60°C. After completion of reaction, the mixture was allowed to react at 80°C. for 1 hour with stirring, and the resultant reaction product was poured in 200 cc of water. The oil phase being separated, the aqueous phase was extended with chloroform.

Analysis—Found: C: 23.0%, F: 69.1%, H: 0.27%  
Calcd: C: 23.2%, F: 68.8%, H: 0.24%  
Other properties:  $\eta_{\text{D}}^{25}$ : 1.3134,  $d_4^{25}$ : 1.76 g/cc

### 3. SYNTHESIS OF



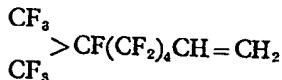
In a flask equipped with a reflux condenser were placed 0.2 mole of



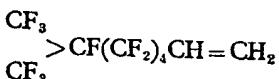
0.2 mole of  $\text{CH}_2 = \text{CH}(\text{CH}_2)_8 \text{COOC}_2\text{H}_5$ , and 0.003 mole of azobisisobutyronitrile. After replacing the air with nitrogen gas, the mixture was stirred at 60° to 70°C. for 7 hours and cooled with water. The unreacted substances were then removed under reduced pressure. To the resultant residue were added 150 cc of ethanol. The mixture was saturated by pass-

The resultant chloroform solution and the separated oil phase put together were dried with anhydrous magnesium sulfate. Fractional distillation after removing the chloroform produced 49.5 grams (0.125 mole) of

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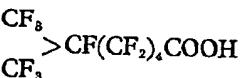


of b.p. 75° to 83° C. under 755 mmHg.  
48 Grams (0.121 mole) of the resultant



were reacted with stirring with a mixture of 74 grams of potassium dichromate, 162 grams of concentrated sulfuric acid, and 58 grams of distilled water at the reflux temperature for 8 hours when there were generated no gases. The reaction product was steam-distilled, and the fractions thus obtained were neutralized with a 5 percent sodium hydroxide aqueous solution and evaporated to dryness. The residue was then placed in excess concentrated sulfuric acid, and distilled under reduced pressure. There were thus obtained 48 grams of

35

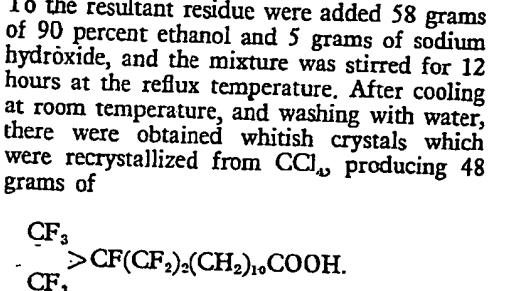


of m.p. -10.5° to -11.0° C. Yield was 95.9 percent by mole.

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ing hydrogen chloride gas. 10 Grams of zinc powder were then added, and the mixture was stirred at 60° to 70° C. for 5 hours. After cooling, the zinc powder was filtered off. The reaction mixture was then poured in 1 liter of water, extracted with chloroform, washed with water, dried with anhydrous magnesium sulfate, and evaporated to remove the solvent. To the resultant residue were added 58 grams of 90 percent ethanol and 5 grams of sodium hydroxide, and the mixture was stirred for 12 hours at the reflux temperature. After cooling at room temperature, and washing with water, there were obtained whitish crystals which were recrystallized from  $\text{CCl}_4$ , producing 48 grams of

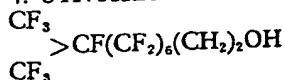
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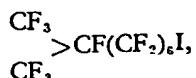
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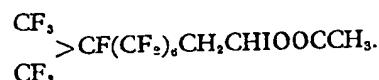
## 4. SYNTHESIS OF



A mixture of 119.2 grams of



5 17.2 grams of purified vinyl acetate, and 0.2 gram of azobisisobutyronitrile was reacted with nitrogen stream at 60° to 80° C. for 6 hours. After cooling to normal room temperature and removing the unreacted iodide of b.p. 69° to 71° C. under 10 mmHg, there were obtained 122 grams of waxy



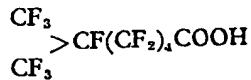
10 The crude iodoacetate thus produced was then dissolved in 170 grams of 75 percent ethanol and the solution was added dropwise for 1 hour to a slurry of 19 grams of 35 percent hydrochloric acid and 38 grams of zinc

Analysis—Found: C: 25.42%, H: 1.01%, F: 70.41%  
Calcd: C: 25.68%, H: 0.97%, F: 70.23%

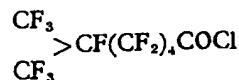
15 For a fuller understanding of the principles of this invention, there are described herein-after the preferred examples which are illustrative only and not limiting the scope and extent of the invention, and in which spray rating was determined in association with the American Association of Textile Chemists and Colorists' standard test method.

## EXAMPLE 1

20 In a 100-cc flask were placed 41.4 grams of

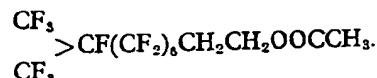


25 and 30 grams of  $\text{SOCl}_2$ , and the mixture was refluxed on a warm water bath for 7.5 hours. The unreacted  $\text{SOCl}_2$  being recovered by distillation at 77° to 79° C., the reaction mixture was distilled under reduced pressure, producing 41.0 grams of

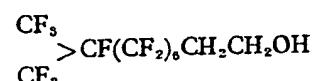


30 of b.p. 54° to 55° C. under 24 to 27 mmHg. Yield was 94.8 percent by weight.

20 powder while being stirred at 60° C. After applying heat and stirring for further 2 hours, the mixture was allowed to cool at room temperature, placed in 200 cc of water, and the oil phase was separated. The aqueous phase was then extracted with chloroform. Fractional distillation of the resultant chloroform solution and the separated oil phase put together produced 95 grams of crude



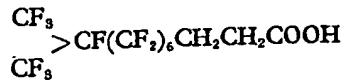
25 The product thus obtained was heated at 60° to 70° C. for about 1 hour with 95 grams of 10 percent by weight potassium hydroxide in ethanol. The mixture was then poured in about 500 cc of water, extracted with chloroform, dried with anhydrous magnesium sulfate, and steam-distilled under reduced pressure, producing 71 grams of



30 of b.p. 100° to 110° C. under 10 to 7 mmHg.

35 0.9 Grams of the compound thus obtained was poured in a flask containing 0.4 gram of a 30 by 70 mm cotton fabric in 6 cc of dimethylformamide, and the content was shaken for a while at room temperature. There was then added 0.5 cc of pyridine. After shaking for about 10 minutes, the cotton fabric was removed out of the flask, rinsed thoroughly with cold water and methanol, and then with water again, and dried at 80° to 90° C. with hot air. The resultant article displayed no changes in the original touch, durability and colour. The total weight was increased by 3 per cent. The water-repellency and oil-repellency were excellent. The same article which was refluxed in  $\text{CCl}_4$  for 2 hours, rinsed with a neutral detergent trade-named 'Monogen' (Daiichi Kogyoseiyou Kabushikikaisha, Japan), and dried at room temperature, completely blocked even the filtration of a 9:1 by volume mixture of n-heptane and liquid paraffin.

40 EXAMPLE 2  
A mixture of 54.2 grams (0.1 mole) of



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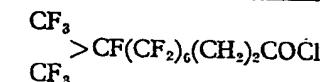
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and 35.7 grams (0.3 mole) of  $\text{SOCl}_2$  was refluxed on a warm water bath for 8 hours. The unreacted  $\text{SOCl}_2$  being recovered by distillation at  $77^\circ$  to  $79^\circ$  C., the mixture was 5 further distilled under reduced pressure, producing



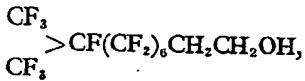
of b.p.  $120^\circ$  to  $130^\circ$  under 0.1 to 0.4 mmHg.

10 Analysis—Found: C: 24.8%, Cl: 6.20%, F: 62.9%  
Calcd: C: 25.7%, Cl: 6.30%, F: 64.4%

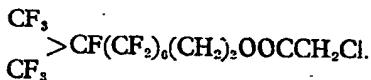
4.5 Grams of the compound thus obtained were poured in a 50-cc flask containing 0.7 gram of cotton gauze dipped in 30 cc of dimethylformamide at  $25^\circ$  C. After violent 15 shaking, there was added 1.7 gram of pyridine and agitated for about 4 minutes. The gauze was then taken out of the flask, thoroughly rinsed with cold water, squeezed, further rinsed with methanol and water, and dried 20 at  $90^\circ$  C. with hot air, producing almost the same original touch and resistance to light. The resultant article sustained water drops about 3 mm in diameter for more than 24 25 hours without causing any substantial disfiguring in the drops, and retained no traces of water after the water drops were removed by tilting the article. Liquid paraffin was also completely repelled.

EXAMPLE 3

30 In a three-neck flask equipped with an agitator, a thermometer and dropping funnel were placed 102.8 grams (0.2 mole) of



heated to  $100^\circ$  C. with a mantle heater, and 35 reacted with 34.0 grams of  $\text{CH}_2\text{ClCOCl}$  added dropwise. Heating and stirring were continued until there was generated no  $\text{HCl}$  gas. The unreacted  $\text{CH}_2\text{ClCOCl}$  being recovered under reduced pressure, the resultant mixture was 40 dissolved in ether, washed with water, and evaporated to dryness on a warm water bath, producing



Analysis—Found: C: 32.5%, N: 4.5%, H: 2.08%, F: 54.1%  
Calcd: C: 31.3%, N: 4.3%, H: 1.59%, F: 55.3%

75 In a 3 percent by weight per volume anhydrous toluene solution of the product thus obtained was dipped a  $30 \text{ cm}^2$  Bavarian cotton fabric for 3 minutes, and the fabric was dried without squeezing at  $70^\circ$  to  $80^\circ$  C., cured at 80  $150^\circ$  C. for 15 minutes, rinsed with a diluted

Analysis—Found: Cl: 5.89%, F: 62.4%  
Calcd: Cl: 6.01%, F: 61.15% 45

10 Grams of the compound thus obtained were dissolved in 60 cc of ether. In the resultant solution was dipped a cotton fabric weighing about 1.5 gram. After thoroughly agitating there were added 2.5 cc of pyridine and heated at the reflux temperature for 1 hour. The gauze was then taken out of the flask, thoroughly washed with water and dried at  $90^\circ$  C. The resultant article displayed an excellent water-repellency and an ability to completely block the infiltration of machine oil. 50 55

EXAMPLE 4  
51.4 Grams (0.10 mole) of

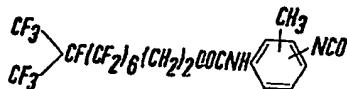


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in 250 cc of anhydrous toluene were mixed with 69.7 grams (0.40 mole) of tolylene diisocyanate and refluxed with heat for 30 minutes under a reflux condenser equipped with calcium chloride drying tubes. After fractionally recovering almost all amount of the toluene employed, the mixture was placed in 100-cc Claisen flask and distilled under reduced pressure to separate the unreacted alcohol and tolylene diisocyanate. Recrystallization from anhydrous toluene produced

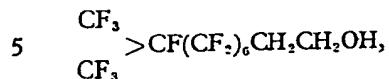
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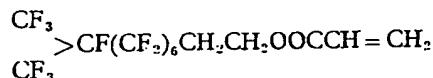


neutral detergent as specified in Example 1 at  $80^\circ$  C. for 20 minutes, and thoroughly dried. The resultant article showed a spray rating of 100, sustained machine oil and liquid paraffin for more than 24 hours, and held vodka drops. 85

**EXAMPLE 5**  
In a 100-cc three-neck flask equipped with a thermometer, an agitator and a reflux condenser were placed 51.4 grams of



1.3 gram of  $\text{BaCl}_2$ , 13.4 grams of acryl chloride, and 0.3 gram of hydroquinone, and the mixture was reacted at  $60^\circ$  to  $70^\circ$  C. for 6 hours. After cooling to room temperature and 10 extracting with chloroform, the chloroform solution was fractionally distilled, producing



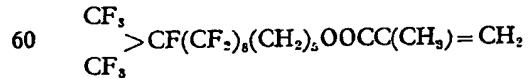
of b.p.  $80^\circ$  to  $85^\circ$  C. under 5 mmHg. Yield was 93.2 percent by weight.

15     Into a 15 percent by weight per volume solution of the resultant product in  $\text{CCl}_4$ , were dipped a  $5 \text{ cm}^2$  cotton gaberdine fabric until thoroughly soaked. The fabric was then framed without squeezing and irradiated for 3 hours 20 with ultraviolet rays emitting from a 400-watt source placed 20 cm apart. The solvent was evaporated during irradiation. After irradiation

45     Analysis—Found: C: 30.91%, F: 62.04%, H: 1.55%  
          Calcd: C: 31.4%, F: 61.3%, H: 1.6%

In a 20 percent by weight per volume solution of the resultant product of  $\text{CF}_2\text{ClCFCl}_2$  was dipped a  $5 \text{ cm}^2$  cotton gaberdine fabric until thoroughly soaked and treated with ultraviolet rays as described in Example 5 to impart water-repellency and oil-repellency. The resultant article sustained machine oil for 3 days without infiltration. The same fabric which was rinsed 3 times with  $\text{CF}_2\text{ClCFCl}_2$  50 and then washed twice with a diluted neutral detergent as specified in Example 1 and dried, exhibited the same results.

55     Almost the same results were obtained with another cotton gaberdine fabric treated with



applied in the same manner as described above.

**EXAMPLE 7**  
In a 20-cc flask were reacted 10 grams of



tion, the article was rinsed with running water and then with warm water at  $40^\circ$  C., and dried at  $90^\circ$  C. The resultant article displayed no changes in the original touch and durability, showing an ability to sustain water drops of 3 to 5 mm in diameter for more than 24 hours and to block the infiltration of the drops of machine oil and naphtha.

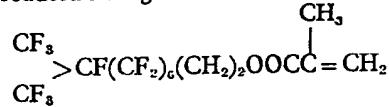
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**EXAMPLE 6**  
In a 200-cc three-neck flask equipped with a thermometer and reflux condenser were placed 51.4 grams of



31.0 grams of methyl methacrylate, 0.6 gram of phenothiazine, and 1.1 gram of concentrated sulfuric acid, and the mixture was reacted with stirring at  $100^\circ$  C. for 10 hours. Fractional distillation of the resultant product produced 54.4 grams of

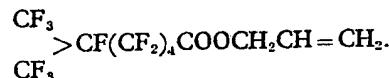


of b.p.  $80^\circ$  to  $85^\circ$  C. under 0.1 mmHg.

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of Example 1 with 1.5 gram of  $\text{CH}_2=\text{CHCH}_2\text{OH}$ , 0.1 gram of  $\text{BaCl}_2$ , and 0.1 gram of hydroquinone at  $60^\circ$  to  $70^\circ$  C. for 4 hours. Fractional distillation of the resultant mixture showed 9.0 grams of

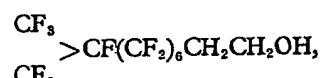


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The cotton fabric treated with the resultant compound as in Example 5 exhibited an excelled water-repellency and oil-repellency.

**EXAMPLE 8**  
In 500 grams of ether dried with metallic sodium were dissolved 205.2 grams of

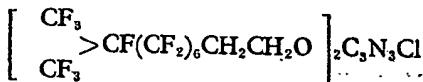


and there were added portionwise 9.3 grams of pulverized metal sodium while cooling with slow stirring to below  $-10^\circ$  C. with a dry ice-methanol refrigerant. The mixture was allowed to react under said conditions for

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further 2 hours. There were then added dropwise for about 2 hours 36.9 grams of purified cyanurylic chloride suspended in 400 grams of dried ether. The temperature was gradually raised to room temperature for 2 hours, and the reaction was continued at the reflux temperature for further 2 hours. After completion of reaction, the mixture was allowed to stand to cool at room temperature, filtered, and evaporated to dryness. Recrystallization from  $\text{CCl}_4$  produced 198 grams of

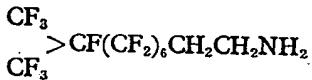


in a state of light yellowish powder.

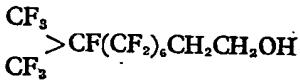
In a 1.5 percent by weight per volume solution of the resultant compound in acetone was dipped a cotton gauze and stirred for about 30 minutes at  $50^\circ\text{ C}$ . while maintaining the pH from 6 to 7 with sodium carbonate added as a hydrochloric acceptor. The gauze thus treated was dried at  $60^\circ\text{ C}$ . for 5 hours, rinsed with a neutral detergent as specified in Example 1, washed with water, and dried at room temperature. The resultant article displayed an agreeable touch and an excellent water-repellency without allowing the water drops quietly applied to infiltrate. Liquid paraffin and naphtha drops were sustained for more than 3 days.

#### EXAMPLE 9

30 In a 2-liter three-neck flask equipped with an agitator and a thermometer were placed 400 cc of acetone, 100 cc of water and 102.6 grams of



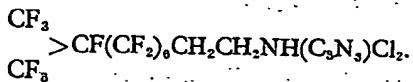
35 which was derived by aminolyzing at  $150^\circ\text{ C}$ .



in 28 percent ammonia water. There were then added while cooling with ice water with violent stirring 40.6 grams of cyanurylic chloride in 200 cc of acetone and 1 kg of ice water. The reaction was continued for about 5 hours while stirring with ice and maintaining the pH at from 6 to 7 with a 10 percent by weight sodium carbonate aqueous solution occasionally added. After filtration, the whitish particles were thoroughly washed with water to remove the unreacted cyanurylic chloride, and dried, producing 1:1 molar addition product

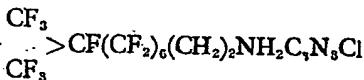
of the starting amine and cyanurylic chloride of the formula

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The compound thus obtained imparted almost the same effects on a cotton gauze as described in Example 8.

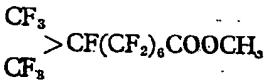
Almost the same results were also obtained with



prepared in the same manner as described above.

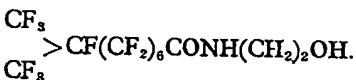
#### EXAMPLE 10

A compound of the formula



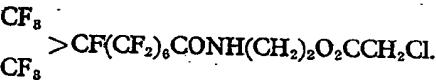
was reacted with an equimolar amount of 2-aminoethanol in ether at  $5^\circ$  to  $10^\circ\text{ C}$ , yielding white solid

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Yield was 98.7 percent by weight. In a 100-cc four-neck flask were then placed 55.8 grams of the resultant product, 11.3 grams of  $\text{CH}_2\text{ClCOCl}$ , and 0.3 gram of copper powder, and the mixture was reacted in nitrogen gas with stirring at  $65^\circ$  to  $70^\circ\text{ C}$ . for 4 hours, producing 44.9 grams of colorless liquid

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Molecular weight in terms of  $\text{C}_{14}\text{F}_{19}\text{O}_3\text{H}_7\text{NCl}$ :

Found:  $632.8 \pm 1.2$ , Calcd: 634.5

Infrared spectrum analysis showed amide absorption at  $5.89\mu$  and ester absorption at  $5.66\mu$ .

In 10 grams of a 7 percent by weight per volume solution of the resultant product in dimethylformamide was dipped 0.95 gram of a cotton gaberdine fabric. There were then added 2 cc of pyridine and thoroughly stirred for 3 minutes. The fabric thus treated was rinsed with water and methanol, and air-dried, producing an excellent resistance to light and durability and a rather soft touch. Spray rating was 100. Machine oil and naphtha drops were held for more than 2 days without infiltration.

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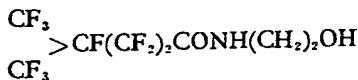
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## EXAMPLE 11

A mixture of 40 grams of

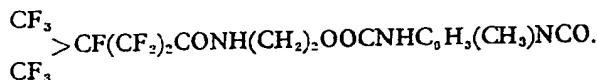


5 prepared in accordance with Example 10, and  
200 cc of anhydrous toluene was warmed to  
40° C. for 3 minutes in a 500-cc flask equipped

with a thermometer and reflux condenser having calcium chloride drying tubes. The mixture was then refluxed with 78 grams of tolylene diisocyanate at the reflux temperature for about 30 minutes. Almost all part of the toluene being removed by distillation, the mixture was heated at 130° to 150° C. under 90 mmHg in a 200-cc Claisen flask to remove the unreacted tolylene diisocyanate. Recrystallization from the toluene and purification yielded 53.1 grams of yellowish crystals of the formula

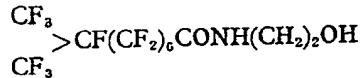
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20 In a 5 percent by weight per volume solution of the resultant compound dissolved in a mixture of ether and toluene was dipped for 5 minutes a hard fibre board consisting of wood cellulose and phenol resins as main components. The article was then predried at 70° to  
25 80° C., thoroughly rinsed with a neutral detergent as specified in Example 1, further rinsed with trichloroethylene for 15 minutes, and dried at 80° C. for 5 hours. The resultant article repelled machine oil and naphtha. Ink drops imparted no traces.

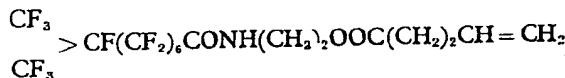
EXAMPLE 12  
Under nitrogen gas were reacted 19.5 grams of



of Example 10 with 4.3 grams of  $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{COCl}$ , 0.1 gram of copper powder, and 0.1 gram of hydroquinone at 75° to 85° C. for 4 hours. Fractional distillation under reduced pressure produced 19.9 grams of

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of b.p. 147° to 156° C. under 1.0 to 2.0 mmHg. Yield was 88.9 percent by weight.

of Example 1, 50 grams of ether, and 6 grams of  $(\text{C}_2\text{H}_5)_3\text{N}$  were reacted with violent stirring in a four-neck flask at -30° to -35° C. with a mixture of 2.4 grams of ethylene imine and 10 grams of ether added dropwise. After completion of reaction,  $(\text{C}_2\text{H}_5)_3\text{NHCl}$  was removed, and the resultant 22.8 grams of

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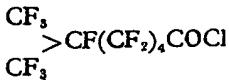
45 Analysis in terms of  $\text{C}_{17}\text{F}_{19}\text{H}_{12}\text{O}_3\text{N}$ :  
Found: C: 33.0%, F: 54.9%, N: 2.41%  
Calcd: C: 31.9%, F: 56.4%, N: 2.19%

50 Into a 15 percent by weight per volume solution of the resultant compound in  $\text{CCl}_4$  was dipped a cotton gaberdine fabric and allowed to stand at room temperature for about 5 minutes. The fabric was then framed and subjected to irradiation of ultraviolet rays for 3 hours emitting from a 400-watt source placed 20 cm apart, linsed with running water, and thoroughly dried at 90° C. The resultant article showed no deterioration in the original touch and durability. Water drops were completely repelled, and machine oil and naphtha were not allowed to infiltrate.

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60 EXAMPLE 13  
24.6 Grams (0.057 mole) of



were stored in dry ice.

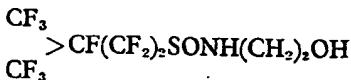
In a solution of 2.5 grams of the resultant compound in 50 cc of  $\text{CFCl}_2\text{CF}_2\text{Cl}$  was dipped a woollen gaberdine fabric weighing 1 gram for 5 minutes, predried at 60° to 70° C. for 3 hours, washed several times with water and a neutral detergent as specified in Example 1, and dried with hot air at 80° C. for 1 hour. The resultant article displayed no deterioration in the original resistance to light, durability and color, although turned rather hard in touch. Spray rating was 100. A 1:9 by volume mixture of liquid paraffin and n-heptane was sustained for 3 days.

75

80

## EXAMPLE 14

18.5 Grams of



5 prepared in accordance with Example 10 were reacted with 9.6 grams of cyanurylic chloride as in Example 8, yielding 24.3 grams of



10 Yield was 94.8 percent by weight. A cotton gauze treated with a 2 percent by weight per volume solution of the resultant compound in acetone, containing 0.5 percent by volume, sustained naphtha without infiltration.



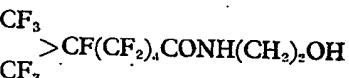
and



15 prepared in the same manner as described above also showed no substantial difference in the resultant excellent oil-repellency.

## EXAMPLE 15

20 A compound of the formula



prepared from



25 in the manner as described in Example 10 was ammonolyzed with 28 percent ammonia water at 150° C. Yield was 83.7 percent by weight.

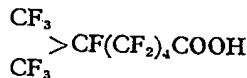
30 To 0.2 mole of the resultant amine in 400 cc of acetone and 100 cc of water placed in a 2-liter three-neck flask was added with violent stirring while cooling with ice water 0.2 mole of cyanurylic chloride suspended in 200 cc of acetone and 1 liter of water, and the reaction was continued in the same manners for 5 hours, the pH being maintained at from 6 to 7 with a 10 percent by weight sodium carbonate aqueous solution added occasionally. After filtration, there were obtained white particles which were washed with water to separate the unreacted cyanurylic chloride, pro-

40 ducing a 1:1 molar addition product of the starting amine and cyanurylic chloride.

45 In a 2 percent by weight per volume solution of the resultant product in acetone containing 0.5 percent by volume of water was dipped at 20° C. a cotton gauze for 1 hour, the pH being kept at from 6 to 7 with a 10 percent by weight sodium carbonate aqueous solution. The gauze was then lightly squeezed, rinsed with a neutral detergent as specified in Example 1, washed with water, and dried. The resultant article showed no coloring and no deterioration in the original durability. Not only water but naphtha and liquid paraffin were sustained for more than 3 days. Almost the same results were obtained on a hard fibre board consisting of wood cellulose and phenol resins when treated in the same manner as described above.

## EXAMPLE 16

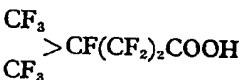
50 A mixture of 10 grams of aluminum powder, 5 grams of



55 and 2 grams of mercuric chloride in 25 grams of isopropyl alcohol was refluxed with stirring at the reflux temperature for 10 hours. The solvent isopropyl alcohol being removed, the residue was rinsed several times with warm water and petroleum ether, and recrystallized with methanol, producing the aluminum salt of said carboxylic acid.

60 In a 3 percent by weight per volume solution of the resultant product in  $\text{CF}_2\text{ClCFCl}_2$  was dipped a cotton gauze for 10 minutes, lightly squeezed, and dried with hot air at 70° C. The resultant article showed almost no deterioration in the original touch. The water-repellency was excellent, and machine oil and naphtha drops were completely sustained.

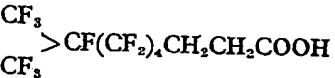
65 The product derived in the same manners as described above from



70 also held machine oil.

## EXAMPLE 17

75 A 2:1:5 by weight mixture of minute aluminum particles,

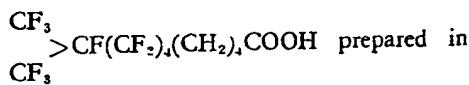


80 and isopropanol was refluxed with mercuric chloride with violent stirring at the reflux temperature for 40 hours. The solvent being

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removed, the residue was thoroughly rinsed with warm water and petroleum ether, producing methanol-soluble white particles of the aluminum salt of said carboxylic acid. A 5 cotton gauze treated as in Example 16 with a 3 percent by volume solution of the resultant product in  $C_2F_3Cl_3$  produced an excellent water-repellency. Naphtha was also sustained without infiltration.

10 Almost the same results were obtained with the aluminum salt of



the same manner as described above.

EXAMPLE 18

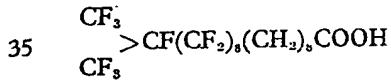
15 To 22 grams of 20 percent by weight of iron chloride placed in a 100-cc three-neck flask were added slowly at room temperature with thorough stirring 69 grams of a 20 percent aqueous solution of



With the advance in reaction, brownish resinous substances precipitated. Stirring was continued for further 30 minutes after completion of addition. In a 3 percent by weight 25 per volume of the resultant resinous iron salt in acetone was dipped a cotton gauze and dried at room temperature. The resultant rather brownish article displayed an excellent water-repellency. Naphtha and machine oil were sustained without infiltration.

EXAMPLE 19

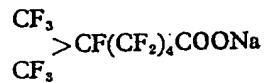
To a 20 percent by weight aqueous solution of ferric chloride was added dropwise with stirring at room temperature



in an almost equimolar amount on the basis of the ferric chloride employed. Stirring was continued for further 30 minutes after completion of addition, and the separated resinous 40 substances were thoroughly washed with water, producing brownish substances soluble in acetone and  $C_2F_3Cl_3$ . Yield was 85 percent by weight. In a 2 percent by weight per volume of the resultant product in acetone were dipped 45 a cotton gauze in the manner as described in Example 18. The brownish article thus prepared sustained not only water drops but naphtha and machine oil for more than 24 hours.

EXAMPLE 20

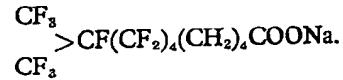
To 117 grams of an aqueous solution containing 0.1 mole of zirconium chloride and placed in a four-neck flask equipped with a thermometer, dropping funnel, an agitator and exhaust pipe were slowly added at room temperature with violent stirring 43.2 grams of



in 200 cc of water. The reaction took place promptly and the content turned jelly. The resultant solids were collected, thoroughly washed with water, and dried at 70° to 80° C. under reduced pressure, producing light yellow waxy solids. Yield was 92.3 percent by weight. In a 1 percent by weight per volume solution of the resultant product in  $CF_2ClCFCl_2$  were dipped a cotton gauze for 3 minutes, dried without squeezing with hot air at 80° C. for 10 minutes, rinsed with water, and thoroughly dried. The article thus prepared showed not only an excellent water-repellency but a pronounced oil-repellency. Naphtha was held for more than 10 hours, and a 8:2 by volume mixture of n-heptane and liquid paraffin was completely repelled.

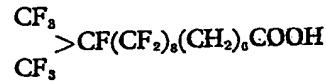
EXAMPLE 21

To a 20 percent aqueous solution of 2 moles of zirconium chloride were added dropwise with stirring at room temperature 2 moles of



The mixture promptly turned jelly. The resultant solids were then separated, washed with water, and dried at 90° to 100° C., producing light yellow waxy substances. Yield was 91 percent by weight. In a 0.5 percent by weight per volume in  $C_2F_3Cl_3$  of the product thus prepared and which was supposedly a multinuclear complex salt was dipped a cotton gauze for 3 minutes, dried without squeezing at 100° C. for 5 minutes, lightly washed with water, and thoroughly dried. The resultant article showed an excellent water-repellency, and sustained liquid paraffin and naphtha for more than 24 hours.

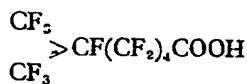
Almost the same results were obtained with the zirconium salt of



prepared in the same manner as described above.

## EXAMPLE 22

5 In a 1-liter 4-neck flask were stirred at  $60^{\circ}$  C. 41 grams of  $\text{CrO}_3$  in 350 grams of water. There was added dropwise a mixture of 320 grams of



10 in 160 cc of methanol. The mixture was refluxed by the exothermic increase in temperature. Stirring was continued for 30 minutes after completion of addition, and the mixture was cooled with water. The resultant slurry precipitates were separated by decantation, washed with warm water at  $40^{\circ}$  to  $60^{\circ}$  C., extracted with ether, filtered, and dried at  $60^{\circ}$  C., producing a chromium salt which was soluble in isopropanol but water-insoluble. In a 1 percent by weight per volume solution of said salt in isopropanol was dipped a nylon gaberdine fabric and dried at  $120^{\circ}$  C. for 20 minutes. The resultant article was light greenish. Spray rating was 100. Naphtha and a 1:1 by volume mixture of n-neptane and liquid paraffin were blocked from infiltration.

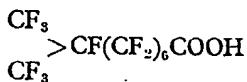
15 20 Almost the same results were obtained with 25 the chromium salt of



prepared in the same manner as described above.

## EXAMPLE 23

30 A mixture of 25.7 grams of



35 in 8 grams of isopropyl alcohol and 300 grams of carbon tetrachloride was refluxed with violent stirring at the reflux temperature. There were then added dropwise 32.5 grams of carbon tetrachloride containing 22.5 grams of chromyl chloride. Stirring was continued for further 2 hours at the reflux temperature. After evaporation on an evaporating dish, the 40 products were condensed at below  $70^{\circ}$  C., producing dark greenish solids which were soluble in acetone, isopropyl alcohol and ether, but hardly soluble in water, although turned water-dilutable when dissolved in acetone or isopropyl alcohol.

45 50 30 Grams of a 20 percent by weight per volume of the resultant chromium salt in isopropyl alcohol were added to 100 cc of water dipping a leather weighing 100 grams, the pH being adjusted to from 3.5 to 4.0 with formic acid. Stirring was continued for about

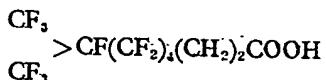
10 minutes until the solution turned colorless. The leather thus treated was washed several times with water, and dried at room temperature. The resultant article showed no deterioration in the original lustre and completely sustained not only water but liquid paraffin and naphtha.

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## EXAMPLE 24

8.9 Grams of

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in 3 grams of isopropanol and 100 grams of carbon tetrachloride were refluxed at the reflux temperature in a flask equipped with an agitator, a thermometer, reflux condenser and dropping funnel. There were then added dropwise 9.0 grams of chromyl chloride in 40 grams of carbon tetrachloride very cautiously not to cause a violent reaction, and the refluxing was contained at the reflux temperature for about 1 hour after completion of addition. When condensed on an evaporating dish at from  $70^{\circ}$  to  $80^{\circ}$  C., there were obtained greenish solids which were soluble in acetone and isopropanol but hardly soluble in water, although turned dilutable with water when dissolved in acetone or isopropanol.

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60 Grams of a 20 percent by weight per volume of the resultant chromium salt in isopropanol were added to 100 cc of water dipping a leather weighing 100 grams, and agitated for 8 minutes until the solution turned colorless. The leather thus treated was thoroughly washed with water, and dried at room temperature. The resultant leather repelled not only liquid paraffin and naphtha without infiltration but water as well.

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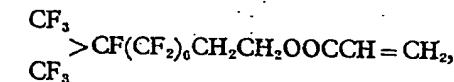
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EXAMPLE 25

In a 500-cc three-neck flask filled with nitrogen gas were reacted with stirring at  $10^{\circ}$  C. for 10 hours 56.8 grams of

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2.2 grams of  $\text{CF}_3(\text{CF}_2)_6\text{COONH}_4$ , 0.07 gram of ammonium persulfate and 0.05 gram of L-ascorbic acid in 220 cc of deoxidized distilled water, producing, when dried, a flexible, colorless latex containing solids by 20 percent by weight. The latex thus prepared was diluted with water to the order of 1 percent by weight. In said emulsion was dipped a woollen gaberdine fabric and allowed to stand at room temperature for 5 minutes. The fabric was then lightly squeezed, predried with hot air, and cured at  $120^{\circ}$  C. for 10 minutes, thoroughly washed with water, soaped with a

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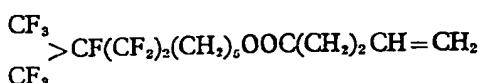
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diluted neutral detergent as specified in Example 1, thoroughly rinsed with water, and dried at room temperature. Spray rating was 100. Machine oil and naphtha were

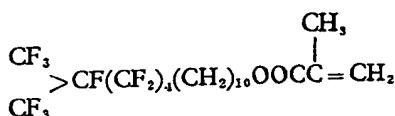
sustained without infiltration for more than 5 days.

Almost the same excellent results were obtained with a polymer emulsion of



10 prepared in the same manner as described above.

Further, a polymer emulsion of

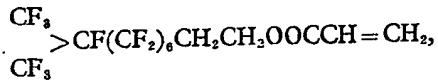


15 prepared in the same manner as described above was diluted with water to the order of 2 percent by weight. In the resultant aqueous emulsion was dipped a filter paper for 3 minutes, skimmed up on a wire net, dried at room temperature, sufficiently washed with water, and dried on the net at room temperature. The resultant article displayed an excellent water-repellency and repelled machine oil.

20

#### EXAMPLE 26

In a 1-liter four-neck flask filled with nitrogen gas were stirred at 50° C. for 1 hour 142 grams of



9.8 grams of maleic anhydride, and 1.5 grams of  $\text{CF}_3(\text{CF}_2)_6\text{COONH}_4$  in 400 cc of distilled water. There was then added dropwise while controlling the rising temperature due to the exothermic reaction, 0.6 gram of potassium persulfate dissolved in 100 cc of distilled water, and the reaction was continued at 50° C. for 20 hours. A violently exothermic reaction took place at the initial stage, but the reaction gradually slowed down, producing a colorless latex containing solids by about 20.1 percent by weight.

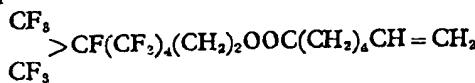
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An emulsion of the resultant copolymer product and maleic anhydride was diluted with water to a concentration of 2 percent by weight and applied to a nylon fabric in the manner as described in Example 25. The re-

45 sultant fabric showed to deterioration in the original touch. Spray rating was 100. Liquid paraffin and naphtha were sustained without infiltration.

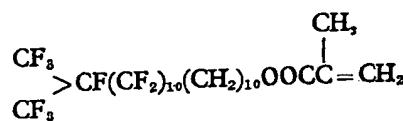
Almost the same results were obtained with 50 an aqueous emulsion of a 5:2 molar copolymer of



and maleic anhydride prepared in the same manner as described above.

#### EXAMPLE 27

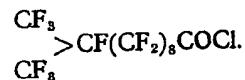
In a 2 percent by weight aqueous solution of a 8:1 molar copolymer of



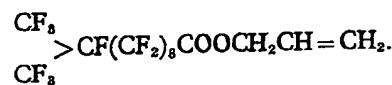
and methyl methacrylate was dipped a fibre board consisting of wood cellulose and phenol resins as main components, predried at room temperature, cured at 150° C. for 5 minutes, washed with water, and dried at room temperature. The resultant article showed an excellent water-repellency and repelled machine oil and liquid paraffin without allowing to leave any trace.

#### EXAMPLE 28

To 12 grams of allyl alcohol and 10 cc of pyridine placed in a flask equipped with a reflux condenser, thermometer, an agitator and a dropping funnel were added dropwise with stirring 60° C. 63.3 grams of

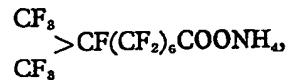


After applying violent stirring for 30 minutes, the mixture was fractionally distilled, producing



Yield was 91.5 percent by weight.

In a 500-cc closed vessel were then stirred at 60° C. for 5 hours 57.0 grams of the resultant compound, 1.8 grams of



3 grams of ammonium persulfate, and 30 grams of acetone in 255 grams of deoxidized distilled water. The resultant aqueous emulsion contained solids by about 16.3 percent by weight.

The emulsion thus prepared was diluted with water to the order of 2 percent by weight. In the resultant emulsion was dipped a woolen gaberdine and a cotton-polyethylene terephthalate fabric for 3 minutes. Each of the fabrics was then lightly squeezed, predried at 70° to 80° C. with hot air, cured at 120° C. for 10 minutes, rinsed with a diluted neutral detergent as specified in Example 1, washed with water and dried at room tem-

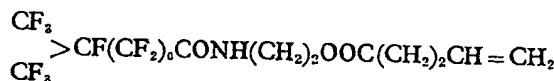
perature. The articles thus obtained completely retained the original touch. Spray rating was 100. The articles also completely sustained a 1:9 by volume mixture of liquid paraffin and n-heptane.

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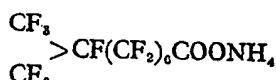
Further, a cotton-polyethylene terephthalate fabric treated in the same manner as described above with a 2 percent by weight polymer emulsion of



prepared in the same manner as described before displayed a spray rating of 100 and sustained a 20:80 by volume mixture of liquid paraffin and n-heptane for more than 25 24 hours.



30 prepared in accordance with Example 12, 8 grams of acetone, and 3 grams of



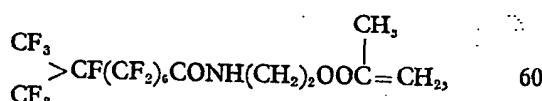
in 200 grams of deoxidized distilled water. The reaction temperature was gradually raised 35 to 50° C. There was then added 1 gram of potassium persulfate in 50 grams of deoxidized distilled water. The reaction temperature was further raised to 60° C., and the mixture was allowed to react at said temperature for further 40 5 hours, producing an emulsion of a polymer concentration of 8.5 percent. In a 1.5 percent by weight aqueous emulsion of the resultant product were dipped a cotton gaberdine fabric, woolen gaberdine fabric, nylon twill and acetate fabric. Said fabrics were then 45 lightly squeezed, predried at 60° to 70° C., cured at 120° C. for 3 minutes, rinsed with a dilute neutral detergent as specified in Example 1, washed with water, and dried at room temperature. Each of the resultant fabrics displayed a spray rating of 100 and 50 sustained a 1:9 by volume mixture of liquid paraffin and n-heptane without allowing infiltration.

55 Almost the same results were obtained with a 1 per cent by weight aqueous emulsion of a polymer of



#### EXAMPLE 29

Under nitrogen gas were reacted with stirring 25 grams of



or of a 50:50 molar copolymer of



and isopropyl acrylate, all being prepared in the same manner as described above.

A further treatment with a conventional pyridinium-type water-repellent composition imparted to the articles treated with the aforesaid compositions of this invention the same order of water-repellency and oil-repellency and improved the resistance to light and dry cleaning to an almost permanent order.

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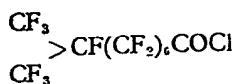
#### EXAMPLE 30

To a solution of 10 grams of polyvinyl alcohol powder of an average polymerization degree of  $550 \pm 50$  and a saponification value of  $88.0 \pm 1.0$  percent (trade-named 'PVA-205,' Kurashiki Rayon Kabushiki-kaisha, Japan) in 150 cc of dimethylformamide in a 500-cc four-neck flask equipped with a reflux condenser, dropping funnel, thermometer and an agitator, were added 22 cc of pyridine. There were then added dropwise

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with stirring at the reflux temperature 200 cc of 107 grams of



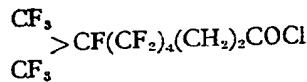
5 in dimethylformamide, and reacted with stirring for 1.5 hour. After removing by distillation almost all part of the dimethylformamide, the residue was thoroughly rinsed with methanol and dried under reduced pressure. The resultant brownish gummy substance was dissolved in  $\text{CF}_2\text{ClCFCl}_2$  to the order of 2 percent by weight per volume. In the solution thus prepared was dipped a cotton gauze for 10 minutes, lightly squeezed, and dried at room temperature. The article thus treated

10 showed a rather sticky touch, completely repelling water and sustained for more than 35 hours a 8:2 by volume mixture of n-heptane and liquid paraffin. The same composition imparted to a fiber board consisting of woollen cellulose and phenol resins as main components a complete water-repellency. Machine oil and naphtha produced no traces.

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20 To 9 grams of polyvinyl alcohol powder as specified in Example 30 and which were dissolved in 300 cc of dimethylformamide in a 500-cc four-neck flask equipped with a reflux condenser, dropping funnel, thermometer and an agitator, were added 20 cc of pyridine. There were then added dropwise 92 grams of

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with stirring at the reflux temperature. The reaction was continued for 1 hour. After recovering by distillation almost all part of dimethylformamide, the residue was thoroughly rinsed with methanol, and vacuum-dried, producing brownish gummy substances soluble in  $\text{CF}_2\text{ClCFCl}_2$ .

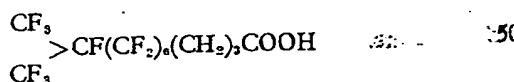
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In a 2 percent by weight per volume solution in  $\text{CF}_2\text{ClCFCl}_2$  of the resultant polyester was dipped a fibre board consisting of wooden cellulose and phenol resins as main components, and dried at room temperature. The article thus obtained completely repelled water and sustained machine oil and naphtha without allowing to leave traces.

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Almost the same results were obtained with the polyester prepared by esterifying polyvinyl alcohol with

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in the same manner as described above.

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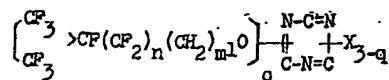
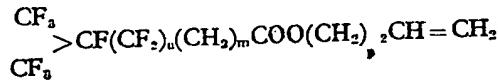
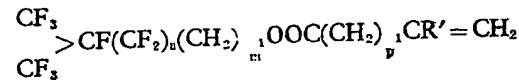
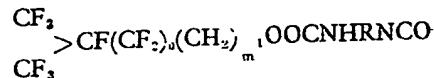
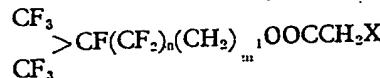
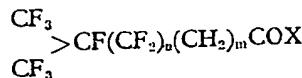
#### WHAT WE CLAIM IS:—

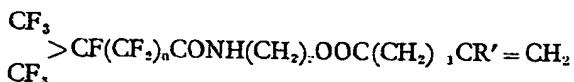
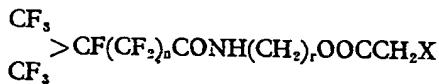
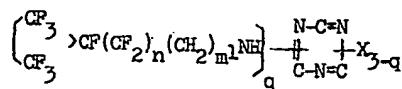
1. A water- and oil-repellent composition comprising at least one fluoroalkyl-containing compound dissolved or suspended in at least one liquid medium; said fluoroalkyl-containing compound being present in an amount of at least 0.1 gram per 100 milliliters of said liquid medium and being selected from the compounds belonging to following Groups A, B, C-1 and C-2:

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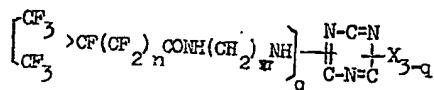
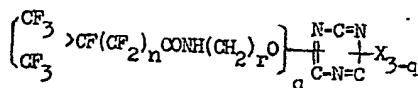
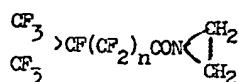
Group A: A fluoroalkyl-containing compound of the formulae:

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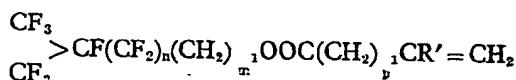
wherein R is a member selected from ,  and  $(\text{CH}_2)_k$  -

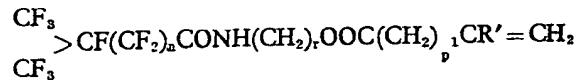
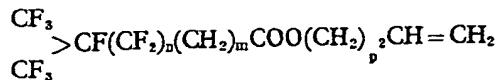
Y being an alkyl having from 1 to 3 carbon atoms, and k being an integer from 2 to 10;

10 R' is a member selected from —H and —CH<sub>3</sub>; CF<sub>3</sub> > CF(CF<sub>2</sub>)<sub>n</sub>(CH<sub>2</sub>)<sub>m</sub>COOH,  
X is a member selected from —F, —Cl, —Br CF<sub>3</sub>  
and —I; wherein n and m are as defined above; 25

n is an integer from 2 to 20; Group C-1: A polymer selected from a  
m is 0 or an integer from 1 to 20; homopolymer of a branched-chain fluoroalkyl-  
15 m<sup>1</sup> is an integer from 1 to 20; containing unsaturated compound; a copolymer  
p<sup>1</sup> is 0 or an integer from 1 to 20; of at least two of said unsaturated compounds;  
p<sup>2</sup> is an integer from 1 to 20; and a copolymer of at least one of said un-  
q is 1 or 2; and saturated compounds in the order of at least 25  
r is an integer from 2 to 10. percent by weight and a polymerizable monomer of other kinds having at least one ethylenic linkage, said unsaturated compound is a member selected from the group consisting of the compounds of the formulas: 30 35

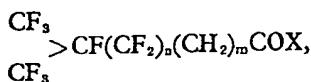
20 Group B: A metallic salt selected from iron, zirconium, aluminum and chromium salts of a fluoroalkyl-containing aliphatic carboxylic acid of the formula





wherein R'; n; m; m'; p'; p'; and r are as defined above and

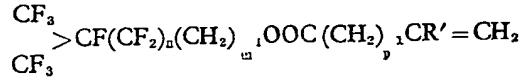
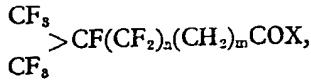
5 Group C—2: A polyester prepared by esterifying the hydroxyl group to the order of from 30 to 100 percent of a polyvinyl alcohol having an average polymerization degree of from 300 to 1,000 and a saponification value of 10 from 70 to 100 percent with an acid halide of the formula



wherein X is selected from —F, —Cl, —Br and —I; n and m are as defined above.

15 2. The water-and oil-repellent composition of Claim 1, wherein said fluoroalkyl-containing compound is at least one member selected from Group A as defined in Claim 1.

20 3. The water- and oil-repellent composition of Claim 2 in which said fluoroalkyl-containing compound is at least one member selected from the compounds of the formula:



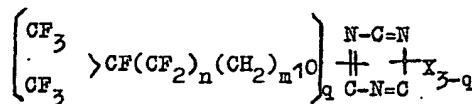
45 wherein R', n, m', and p' are as defined in Claim 1.

7. The water- and oil-repellent composition



wherein n; m; and p' are as defined in Claim 1.

55 8. The water-and oil-repellent composition of Claim 2 in which said fluoroalkyl-containing compound is at least one member selected from the compounds of the formula:

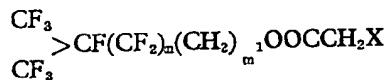


wherein n; m' and q are as defined in claim 1.

9. The water- and oil-repellent composition

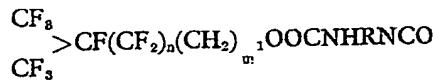
wherein X; n and m are as defined in Claim 1.

4 The water-and oil-repellent composition of Claim 2, in which said fluoroalkyl-containing compound is at least one member selected from the compounds of the formula:



wherein X; n and m' are as defined in Claim 1.

5 The water-and oil-repellent composition of Claim 2, in which said fluoroalkyl-containing compound is at least one member selected from the compounds of the formula:

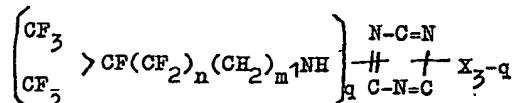


wherein R, Y, k, n, and m' are as defined in claim 1.

6. The water- and oil-repellent composition of Claim 2, in which said fluoroalkyl-containing compound is at least one member selected from the compounds of the formula:

of Claim 2, in which said fluoroalkyl-containing compound is at least one member selected from the compounds of the formula:

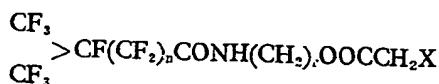
of Claim 2, in which said fluoroalkyl-containing compound is at least one member selected from the compounds of the formula:



wherein n; m'; q are as defined in claim 1.

10. The water- and oil-repellent composition of Claim 2, in which said fluoro-con-

taining compound is at least one member selected from the compounds of the formula:



wherein X; n; and r are as defined in claim 1.

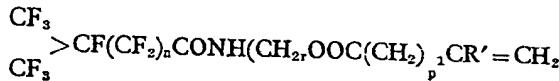
11. The water- and oil-repellent composition of Claim 2, in which said fluoroalkyl-containing compound is at least one member selected from the compounds of the formula:



10 wherein R, Y, k, n and r are as defined in claim 1.

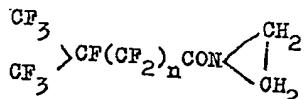
12. The water- and oil-repellent composition

of Claim 2, in which said fluoroalkyl-containing compound is at least one member selected from the compounds of the formula:



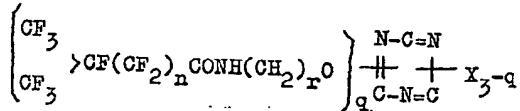
wherein R'; n; r; and p<sup>1</sup> are as defined in Claim 1.

13. The water- and oil-repellent composition of Claim 2, in which said fluoroalkyl-containing compound is at least one member selected from the compounds of the formula:



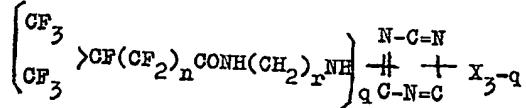
25 wherein n is an integer from 2 to 20.

14. The water- and oil-repellent composition of Claim 2, in which said fluoroalkyl-containing compound is at least one compound selected from the compounds of the formula:



30 wherein X; n; r; and q are as defined in claim 1.

15. The water- and oil-repellent composition of Claim 2, in which said fluoroalkyl-containing compound is at least one member selected from the compounds of the formula:

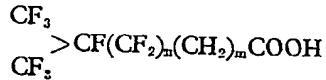


wherein X; n; r; and q are as defined in claim 1.

16. The water- and oil-repellent composition of Claim 2, in which said liquid medium is at least one species of solvent selected from toluene, acetone, ether dimethylformamide and trichlorotrifluoroethane.

17. The water- and oil-repellent composi-

tion of Claim 1, in which said fluoroalkyl-containing compound is at least one metallic salt selected from chromium, zirconium, aluminum and iron salts of an aliphatic carboxylic acid of the formula:



wherein n; and m are as defined in claim 1.

18. The water- and oil-repellent composition of Claim 17 in which said metallic salt is an iron salt.

19. The water- and oil-repellent composition of Claim 17, in which said metallic salt is a zirconium salt.

20. The water- and oil-repellent composition of Claim 17, in which said metallic salt is an aluminum salt.

21. The water- and oil-repellent composition of Claim 17, in which said metallic salt is a chromium salt.

22. The water- and oil-repellent composition of Claim 17, in which the liquid medium to be employed is at least one species of solvent selected from aliphatic alcohols having from 1 to 4 carbon atoms, and trichlorotrifluoroethane.

23. The water- and oil-repellent composition of Claim 17, in which said metallic salt is a water-soluble chromium salt and the liquid medium to be employed is water.

24. The water- and oil-repellent composition of Claim 1, in which said fluoroalkyl-containing compound is at least one species of polymer selected from the group C-1 defined in claim 1.

25. The water- and oil-repellent composition of Claim 24, in which the branched-chain fluoroalkyl-containing unsaturated compound from which the polymer is derived is of the formula:

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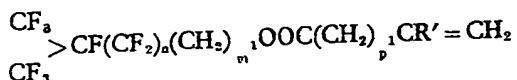
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wherein R'; n; m'; and p<sup>1</sup> are as defined in claim 1.

26. The water- and oil-repellent composition of Claim 24, in which the branched-chain

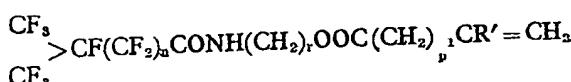
fluoroalkyl-containing unsaturated compound from which the polymer is derived is of the formula:

10 wherein n; m; and p<sup>2</sup> are as defined in claim 1.

27. The water- and oil-repellent composition of Claim 24, in which the branched-chain

fluoroalkyl-containing unsaturated compound from which the polymer is derived is of the formula:

15.



wherein R'; n; p<sup>1</sup>; and r are as defined in claim 1.

20 28. The water- and oil-repellent composition of Claim 24, in which the liquid medium to be employed is at least one member selected from acetone, ether and trichlorotrifluoroethane.

25 29. The water- and oil-repellent composition of Claim 1, in which said fluoroalkyl-containing compound is a polyester of the group C-2 defined in claim 1.

30 30. The water- and oil-repellent composition of Claim 29, in which the liquid medium to be employed is at least one member selected from acetone, ether and trichlorotrifluoroethane.

31. A fluoroalkyl-containing compound selected from the compounds belonging to Groups A, B, C-1 and C-2 of Claim 1.

32. A water- and oil-repellent composition substantially as described in any of the specific Examples herein.

33. A fluoroalkyl-containing compound according to claim 31 and as described in any of the specific Examples herein.

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